Content Enrichment Programme for Tribal School Key Resource Persons of Chhattisgarh in Chemistry at Senior Secondary Level.

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एनसीईआरटी
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DR. R.S.SINDHU
Programme Coordinator

REGIONAL INSTITUTE OF EDUCATION
(National Council of Educational Research and Training)
Bhopal – 462013.

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Foreword

At the completion of ten years of general education the students move towards diversification at the senior secondary stage. This stage attains special significance because for majority of the students this may be the end of their formal education thereby leading them to the world of work. For others, it works as a bridge to the tertiary stage of education – academic or professional. Due to discipline orientation of the curriculum, the teachers are required to be masters in their own subjects of specialization. With the advent of cybranetics the subject area of Chemistry has attained tremendous growth resulting in modernized content which need to be discussed and assimilated by the teachers so that they are able to do justice to the subject matter content in the classrooms. This obviously calls for periodical inservice refresher programmes to be conducted by specialized institutions like Regional Institute of Education. In keeping with the cascade mode of training, the RIE, Bhopal took up this content enrichment programme for tribal school Key Resource Persons of Chhattisgarh to enrich them with the latest content.

In this programme, the hard spots of the Chemistry Syllabus as well as the newly introduced topics were identified both in theory and practicals. The Resource Persons drawn both from the Institute and outside provided inputs in these identified areas during the 5-days programme. The KRPs were also familiarized with the use of information and communication technology in transacting the Chemistry Curriculum

Dr. R.S. Sindhu, the Programme Coordinator deserves special thanks for successfully completing the programme and bringing out the Report in the present form. Thanks are also due to all the Resource Persons. The trained KRPs can now be expected to train in turn many more teachers in the State.

M. Sen Gupta
Principal

Acknowledgements

Preface

Chemistry is an elective subject at Senior Secondary level Students at this stage switch from general education to discipline oriented education The discipline of chemistry expands horizontally as well as vertically at this stage. Some of the concepts are hard in understanding, some new concepts have been incorporated in the syllabus and different formulations, nomenclature and units of data have been introduced In the area of instructional materials, information and communication technology is available which can effectively improve instructional process Keeping above aspects in view, the present programme has been formulated to train the Tribal School Key Resource Persons (KRPs) of Chhattisgarh, teaching chemistry at Senior Secondary Level

A questionnaire was developed to identify new areas of chemistry, hard spots in teaching-learning and instructional materials used by the teachers. The teachers had given their responses These responses were analyzed and on the basis of analysis, the input to be given to the KRPs in the training programme of five day's duration was finalized

The training programme was organized from 23rd August to 27th August, 2004 at Regional Institute of Education, Bhopal. In all 19 participants attended the programme These participants are employed in different tribal schools of Chhattisgarh State Seven resource persons, three from Regional Institute of Education and four from outside Institutions were involved in training the participants. The resource persons have expertise in different fields of chemistry and training modes

During the programme the KRPs were exposed to different sessions related to identified areas of chemistry Some sessions were devoted to instructional materials and practical work also Each session was, mainly, of interactive mode The experiences of RPs and KRPs were shared and clarifications made wherever needed

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this stage. Different types of hybridization viz sp^3, sp^2 and sp may be taken up at this level only by discussing the shape of organic molecules like C_2H_6, C_2H_4 and C_2H_2 after discussing the shape of simple molecules like CH_4 and CCl_4

While discussing tetravalence of carbon, it may be highlighted at this stage that C is to be bonded either to four monovalent atoms like F, Cl, Br, I, H or monovalent groups like $-NH2$, $-NO_2$, -OR etc. Carbon can be jointed to another carbon through single bonds as in alkanes (-C-C-C-C- or C-C) or through double bonds as in alkenes (C=C, C-C=C C-C=C-C) or through triple bonds as in alkynes (C≡C-, C≡C-C etc) The remaining valances of C are to be satisfied by joining the requisite number of hydrogen atoms to the C atoms

Carbon may also be bonded to oxygen either through double bonds as in
$$R-C=O, \quad R-C=O$$
$$\begin{array}{cc} | & | \\ H & R \end{array}$$

Or through single and double bonds as in
$$-C-O-H \text{ or } -C-O-R, \text{ or } -C-NH_2 \text{ or}$$
with O (double bond, ‖) above each C

-C-N-R (with O double bond ‖ and H above). Students have been found committing mistakes in writing alcohols and carboxylic acids as R-H-O and R-C=O-H with O below. Such types of mistakes are to be highlighted and may be Checked in the beginning stage only. It may also be emphasized that H is monovalent, oxygen is bivalent and N is trivalent in most of the organic compounds

Sp^2 hybridization in benzene may also be discussed at this stage The concept of resonance and delocalisation of π electrons will help the students to understand the resonating structures of benzene accounting for its unique behaviour Regular tetrahedral shape of molecules like CH_4, CCl_4 etc will also account for non-polar nature of the molecules As there is only a single P G T (Chemistry) in Hr Secondary School irrespective of the branch specialization, it would be in the fitness of things to discuss hybridization and shapes of inorganic molecules like BF_3, BeF_2, NH_3 and H_2O at this stage only Polar and non-polar nature and difference in bond angles in different molecules may also be discussed at this level

3. Nomenclature and Isomerism

As already stated, majority of the students and the teachers are found committing mistakes in writing names of the compounds Hence, there is a need for an intensive practice on identifying isomers and naming the members of different homologous series (Ferfuson, 1975, Eliel, 1982) It is the general practice that teachers discuss 3-4 homologues series of alkanes, alkenes and alkynes in one period only and the rest are left to the students We are building foundation of students in a new branch of Chemistry and this foundation is to be very strong It is, therefore, suggested that teachers discuss both common and IUPAC systems of naming of different compounds in detail Naming should be discussed one by one with the help of students Teachers may discuss upto 5-6 members of each homologous series While discussing nomenclature of different series, students may be asked to write structures of different isomers corresponding to any molecular formula Emphasis may also be laid on different possibilities of writing structures corresponding to the general formula of any homologous series by changing value of n i e number of C atoms in a molecule As we go ahead, there may be more than one arrangements (Structures or configurations) of atoms/groups leading to the concept of

isomerism   Misconceptions regarding definition of isomerism may be classified at this stage.   Writing of difference possible structures/configurations corresponding to one general formula may be practised by students   After writing different possibilities, they may be asked to name them in both the systems of nomenclature i e common and IUPAC Different pairs of compounds and type of isomerism shown by them may also be identified Thus sequential development of tetravalency of carbon, hybridization, shapes of molecules, nomenclature of different members of different homologous series will help the students in learning of organic chemistry   This point can be brought home by taking up the following exercise as given below in the box

> **Write structures of different isomeric compounds corresponding to the m.f. (i) $C_4H_{10}O$ (ii) $C_4H_{11}N$. Write IUPAC names of all the compounds. What type of isomerism is exhibited by different pairs?**

After discussing nomenclature of compounds of difference homologous series, rules for nomenclature of complicated compound may also be discussed These rules may then be applied on naming of different compounds   The following exercise may be useful in strengthening the understanding of nomenclature

Write IUPAC names of the following compounds·

1. $(CH_3)_2\ NOCH$

2   $C_2H_5COOCH_3$

3   $C_2H_5OOCCH_3$

4   $CH_3OCH\ (C_2H_5)_2$

5   $CH_3\ (CH_2)_2\ N\!\!\begin{array}{l} {}^{\diagup CH_3} \\ {}_{\diagdown C_2H_5} \end{array}$

6   $CH_3\ (CH_2)_4\ CHCNCH_3$

Names of compounds like $CH_2 = CH - \underset{\bighexagon}{C} = CH_2$ and $CH_2 = CH - \underset{\bighexagon}{C} = CH_2$ may also be tried and difference between phenyl and cyclohexyl group may be highlighted It would be interesting to try names of compounds like $CH_3OCH_2CH_2CH_2CH_3$, $CH_3OCH\ (CH_3)_2$, $C_2H_5NH\ CH\ (C_2H_5)_2$ and $(CH_3)_3\ COH$ It may be remembered that you may not get the correct name unless you open the bracket

Naming of bicyclo compounds

According to the IUPAC system, cycloalkanes consisting of two rings only and having two or more atoms in common, the prefix bicyclo is used followed by the name of the alkane containing the same total number (Finar, 2001) The number of carbon atoms in each of the three bridges connecting the two tertiary carbon atoms is indicated in brackets in descending order. Numbering begins with one of the bridgeheads and proceeds by the longest possible path to the second bridgehead, numbering is then continued from this atom by the longer unnumbered path back to the first bridgehead and is completed by the shortest path

3

Names of the following compounds can be tried

CH

$H_2C - CH - CH_2$

bicyclo (1,1,0) butane

CH ——— CH_2

H_2C

CH_2

CH ——— CH_2

bicyclo (3,1,0) hexane

CH

H_2C CH_2

CH

H_2C CH_2

CH

bicyclo (2, 2, 1) heptane

CH_3

$^7CH_2$ —— C —— $^2CHC_2H_5$

$^8CH - CH_3$ $^3CH_2$

^6CHCl —— ^5CH —— $^4CH_2$

6 – chloro – 2 – ethyl – 1, 8 dimehyl
bicyclo (3, 2, 1) octane
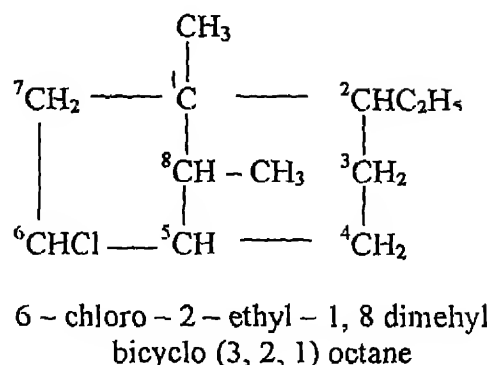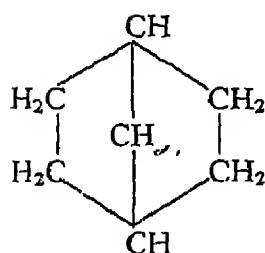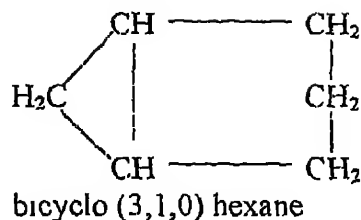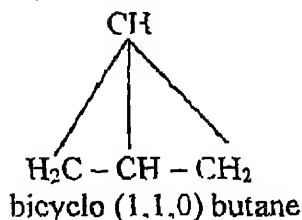
4. Electronegativity

The concept of electronegativity helps in understanding nature of covalent bond in organic molecules and the extent of ionic nature of the bond   The electron cloud that builds two atoms is not symmetrical except when the two atoms are the same and have the same substitutes. The cloud is necessarily distorted towards one side of the bond or the other depending on which atom (nucleus plus electrons) maintains the greater attraction for the cloud This attraction is called electronegativity, it is the greatest for atoms of elements in the upper right corner of the periodic table and lowest for atoms in the lowest corner Thus a bond between fluorine and chlorine is distorted so that there is a higher probability of finding the electron near the fluorine than near the chlorine, which gives the fluorine a partial negative charge. The electronegativities of a few common elements as per pauling scale are given below

Table –1 Electronegativity values of Elements

1.0	1 5	2 0	2 5	3 0	3 5	4 0
Li	Be	B	C	N	O	F
0 9	1 2	1 5	1 8	2 1	2 5	3 0
Na	Mg	Al	Si	P	S	Cl
0 82						2 8
K						Br

Groups have also been assigned the electronegativity values   The electronegativity values of a few groups are given below

Table 1.2   Electronegativity values of groups relative to H (2.176)

— CH₃	2.472	-C Br₃	2 561	- C₆H₅	2 917
C₂H₅	2 482	- CHCl₂	2 602	- CF₃	2 985
— CH₂-Cl	2 538	- CCl₃	2 666	- NO₂	3.421

5.   Basics of Reaction Mechanism

Knowledge of different steps involved in any reaction, conversion of reactants into products, idea of slowest step and rate of consumption of reactants or formation of products constitute what we call reaction mechanism i e reaction mechanism helps us in understanding progress of the reaction in terms of different steps involved in the reaction. Role of a catalyst in many reactions can also be understood well in terms of mechanism For example, how does aluminium chloride act as a catalyst during chlorination, alkylation and acetylation of benzene and other related compounds is explained with the help of mechanism? How is carbocation formed during acidic dehydration of alcohol and why the rate of dehydration of tertiary alcohol is fastest can be understood only by studying mechanism of the reaction Similarly, formation of a carbanion during aldol condensation and Perkin reaction can be interpreted by understanding mechanism of the reactions Reasons for alkyl halides to undergo nucleophilic substitution reactions easily and aryl halides not to undergo nucleophilic substitution reactions so easily can be found only in terms of reaction mechanism Similarly, there are many more reactions at the senior secondary level, which are very difficult to understand without mechanism Students' poor knowledge and understanding of these concepts related reactions lead them to cram and commit mistakes in the examination Hence, it is essential to have an elementary idea of reaction mechanism to fulfill the needs of Sr. Secondary level students as a supplementary teaching learning material to facilitate learning of various reactions of organic chemistry by studying the following concepts·

1.   Concepts

- Bond Fission
- Nature of Attacking Reagents

a) Nucleophiles   b) Electrophiles

Understanding of these concepts may help the readers to seek answers of many reactions at the senior secondary level A brief description of these concepts is given below Mechanism of different reactions can be better understood in the related units as given in the text

5.1   Bond Fission

Let's consider a general reaction

$$R - X + Y \rightarrow R - Y + X$$

From the above reaction, it is amply clear that the old linkage between R and X is cleaved and the new bond between R and Y is established It will depend upon the reaction environment i.e nature of $R - X$ molecule, the attacking reagent (y) and the reaction conditions to decide whether bond fission and bond formation take place simultaneously or in consecutive steps The single covalent bond in $R - X$ molecule can undergo fission in the following two ways

5.1.1 Homolysis

The single convalent bond formed by sharing of two electrons from R and X may undergo fission in such a manner so that each of the constituent retains one electron Such a type of fission is known as homolysis and the entities thus obtained are known as free radicals

$$R - X \xrightarrow{E\, =\, h\nu} R. + .X$$

$$Cl - Cl \longrightarrow Cl. + .Cl$$

$$H - H \longrightarrow H. + .H$$

$$\begin{array}{ccc}
& H & & H \\
& | & & | \\
H - & C & - H \longrightarrow H - & C. & + \;.H \\
& | & & | \\
& H & & H \\
& \text{Methyl} & & \text{Hydrogen} \\
& \text{Free radical} & & \text{free radical}
\end{array}$$
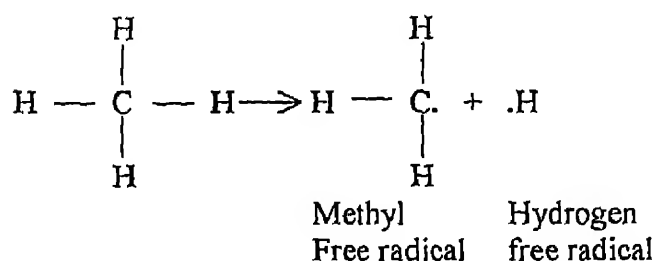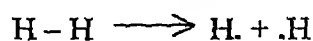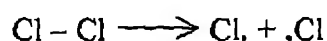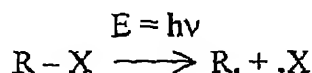
5.1.2 Characteristics of Free Radicals

- Free radicals are the entities/fragments obtained by the homolytic fission of a bond
- They are known as free radicals because they have free electrons
- They are odd election species i e an unpaired electron is present
- As the free radicals carry their own electron. they are electrically neutral
- Free radical may be an individual atom or a group of atoms
- They are highly unstable due to the presence of a free electron

Reactions involving free radicals are known as free radical chain reactions and their mechanism is known as the free radical chain mechanism This can be illustrated by taking an example of chlorination of methane while studying hydrocarbons

5.2 Heterolysis

Fission of the bond can also take place in a manner where the shared electron pair is retained by one of the two constituents It will again depend upon the reaction environment and the nature of the two groups in the molecule i.e which of the constituents retains the shared electron pair. Such a type of fission is known as heterolysis or heterolytic fission This may result in the formation of carbocation or Carbonanion depending upon the reaction conditions

5.2.1 Formation of Carbocation ($\diagdown\!\!\diagup C^{+}$)

Carbocation is formed when the shared electron is retained by X (X is not necessarily halogen atom) and not by R as shown below.

$$R - X \longrightarrow R^+ + X^-$$

Carbocation

(R is an alkyl or aryl group)
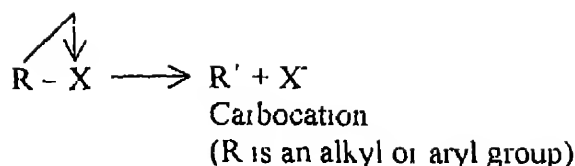
Carbocations are obtained as reaction intermediates in many reactions like halogenation, nitration, sulphonation, Friedel-Craft alkylation and accetylation of arenes, acidic dehydration of alcohols, hydrolysis of tertiary alkyl halides etc It can be termed as primary, second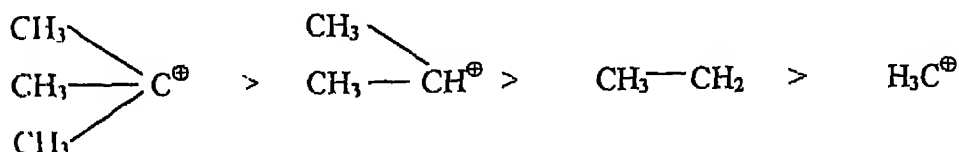ary or tertiary depending upon the fact whether the positive charge lies on the primary, secondary or tertiary Carbon ion as shown below

$$\overset{\text{\textbullet}}{CH_3},\qquad CH_3 - \overset{+}{CH_2},\qquad \underset{CH_3}{\overset{CH_3}{\diagdown}}\overset{+}{CH},\qquad \underset{CH_3}{\overset{CH_3}{\diagdown}}CH_3\!-\!C+$$

Methylium ion	Ethylium ion	Isopropylium ion	Tertiary Butyl
or	or	or	Carbocation
Methyl	Ethyl Carbocat	Isopropyl	(Tertiary)
Carbocation	-ion (Primary)	Carbocation	
(Primary)		(Secondary)	
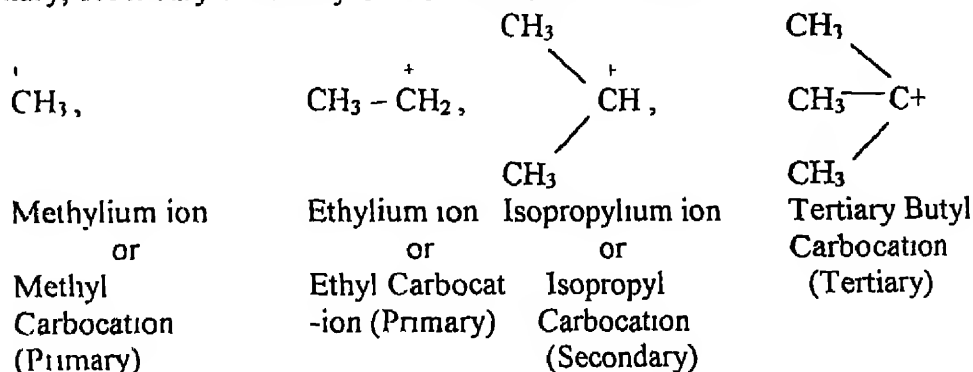
5.2.2 Characteristics of Carbocation

- Carbocation is obtained by hetrolysis of a bond
- Carbocation is electron deficient ion and carries +ve charge
- It is sp2 hydridised
- It is unstable but can be stabilized if some electron donating group (alkyl group) is attached to (+ Inductive effect) it The stability order of different Carbonium ions is given below

$$\underset{CH_3}{\overset{CH_3}{\diagdown}}\!\!\!\!\!\underset{CH_3}{\diagup}\!\!\!C^{\oplus} \;>\; CH_3\!-\!\underset{CH_3}{\overset{CH_3}{\diagdown}}CH^{\oplus} \;>\; CH_3\!-\!CH_2 \;>\; H_3C^{\oplus}$$

In tertiary butyl carbocation, three methyl groups are attached to the Carbocation Due to the electron donating nature of methyl groups, the shared electron pairs between +vely charged Carbon and the three methyl groups are slightly displaced towards the positively charged carbon ion as a result of which the electron deficiency is compensated to some extent and hence stability This effect is known as +I effect (Inductive) because the electrons are shifted away from the methyl groups

Carbocation can also be stabilized as a result of resonance More the resonance, more the stability. This aspect will be discussed in detail later on while discussing mechanism of reactions

5.2.3 Formaton of Carbanion $(\overset{\diagdown}{\underset{\diagup}{C:}}^-)$

Carbanion is also formed by the hetrolysis of bond but when the shared electron pair is retained by Carbon atom of the alkyl or aryl group R and not by X

$$R \overset{\curvearrowleft}{\underset{\frown}{}} X \longrightarrow R:^- + X^+$$

Carbanion (R – is an alkyl or aryl group)

Aldol condensation and perkin reaction are the common examples in which carbanion is formed as a reaction intermediate.

### 5.2.4 Characteristics of Carbanion

- Carbanion is obtained by heterolysis of a bond
- Carbanion is electron rich and carries negative charge
- Carbanion is unstable due to excess of electron population but can be stabilized if some electron withdrawing atom/group like F atom, NO_2, $\diagdown C = O$, $- C \equiv N$ group is attached to it.
- Carbanion is sp^3 hybridised

5.3 Nature of attacking reagents

Nature of attacking reagent also decides path of the reaction The attacking reagent may be electron rich or electron deficient If the attacking reagent is electron rich, it will attack the reactant molecule (substrate) in a manner so as to generate the carbocation On the other hand, electron deficient reagent will tend to generate a carbanion This forms the basis of attacking reagents to be termed as electrophiles or electrophilic reagents (electrons loving) or nucleophiles or nucleophilic reagents (nucleus loving)

5.3.1 Electrophilic Reagents

If the attacking reagent is of the type y+, i e electron deficient, it will be constantly in search of centre of high electron population Being in search of electrons, such reagents are termed as electrophiles or electrophilic reagents

$$R - X \xrightarrow{\;Y^+\;} R_- + {}^+X$$
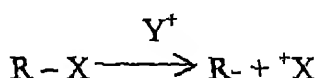
$^+NO_2$ (Nitronium ion), Cl^+ (Chloronium ion), $^+CH_3$ (Methylium ion), $CH_3 - CH_2 +$ (Ethyl Carbocation), $CH_3-C^+=O$ (acetylium ion), etc are the examples of electrophilic reagents. It is not necessary that the electrophiles must carry +ve charge Reagents like BF_3 and $AlCl_3$ in which octet rule is not satisfied, are also in search of centres of high electron density and hence fall in the category of electrophiles Reactions involving electrophiles are known as electrophilic reactions. Depending upon whether addition or substitution is taking place, reactions are termed as electrophilic addition or electrophilic substation reactions. Additions reactions of alkenes and Alkynes are the examples of electrophilic addition reactions as they are the sources of mobile or loosely held π electrons Substitution reactions of benzene, toluene, phenol, benzalhehyde etc are the examples of electrophilic substitution reasons generally designated as S_E
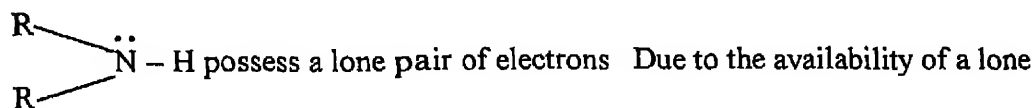
5.3.2 Nucleophilic Reagents

If the attacking reagent is of the type $\bar{y}$, it will be constantly in search of a centre of low electron density   Such reagents are called nucleophiles or nucleophilic (nucleus loving) reagents

$$R-x \xrightarrow{\;\;\bar{y}:\;\;} R-y + \bar{X}$$
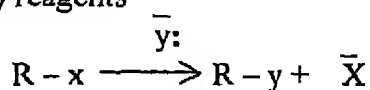
$\bar{C}N$, $\bar{O}H$, $\bar{C}l$, $\bar{B}r$, $\bar{I}$ are a few examples of nucleophilic reagents

Nucleophiles can be neutral molecules also   For example, $\ddot{N}H_3$, $R-\ddot{N}H_2$ or $R_2\ddot{N}H$

$R\diagdown$
$\quad\quad\ddot{N}-H$ possess a lone pair of electrons   Due to the availability of a lone
$R\diagup$

Pair of electrons, these reagents are also in search of centres of low electron cloud Hence, such reagents are also called nucleophiles or nucleophilic reagents

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Classify the following into electrophiles and nucleophiles:
RNH_2, $RCOCl$, BF_3, $\bar{O}H$, CH_3^+, $(CH_3)_2\,CH^+$, NH_3 and $AlCl_3$

Like electrophiles, nucleophiles can participate in addition as well as substitution reactions   If a nucleophile is involved in an addition reaction, the reaction is termed as nucleophilic addition reaction   However, the reaction will be termed as nucleophilic substitution reaction if the nucleophiles is involved in substitution reactions   Addition reactions of aldehydes and ketones fall under the category of nucleophilic addition reactions whereas substitution reactions of alkyl halide are the examples of nucleophilic substitution reactions and designed as S_N.

Electronic Effects

Displacement of electron in covalent-bonded molecules may take place in the four following ways, which determine the course of a reaction

(i)   Inductive effect
(ii) Electromeric effect
(iii) Resonance or mesomeric effect and
(iv) Hyperconjugation

A brief idea about these effects should be given to the students, which will be helpful to seek solutions of many of problems in chemistry
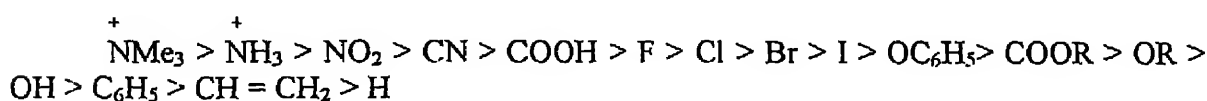
6.1   Inductive Effect

Inductive effect is the permanent displacement of electrons, along the covalent bond from the less electronegative to the more electronegative atom or group resulting in polarity in the molecule   The atom towards which the electron is displaced develops a partial negative charge ($\delta-$) and the atom from which the electron is displaced develops a
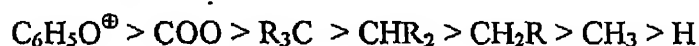
partial positive charge (δ+) The atom, which develops the partial positive charge, pulls the shared electron pair towards itself from the neighbouring atom which develops still smaller positive charge i e $\delta\delta^+$ and thus this induction goes on but the extent of pulling capacity also goes on decreasing and becomes almost zero or negligible beyond 3rd carbon atom This effect is indicated by $\Rightarrow$ and is denoted by I Electron withdrawing groups like - C_6H_5, - NO_2, - $C \equiv N$, F, NMe_3 are said to possess $-I$ effect as they are attracting electrons towards themselves whereas electron releasing groups like $-CH_3$, $-C_2H_5$ etc are said to possess the $+I$ effect

The trend of decreasing order of -I effect and +I effect is given below

(a) Decreasing order of –I effect –

$\overset{+}{N}Me_3 > \overset{+}{N}H_3 > NO_2 > CN > COOH > F > Cl > Br > I > OC_6H_5 > COOR > OR > OH > C_6H_5 > CH = CH_2 > H$

(b) Decreasing order of +I effect

$C_6H_5O^{\oplus} > \overset{.}{C}OO > R_3C > CHR_2 > CH_2R > CH_3 > H$

6.2. Electromeric Effect

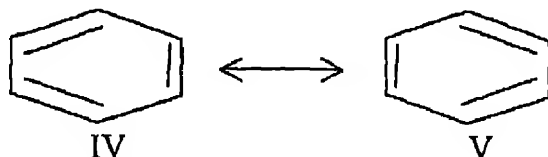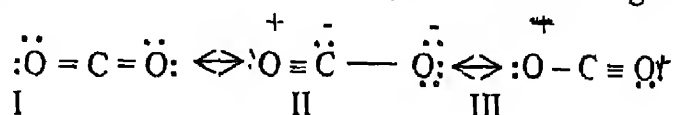Electromeric effect involves the complete migration of electron from the less electronegative to more electronegative atom or group This is a temporary effect and comes into play only at the requirement of the attacking reagent and ceases to operate the moment the attacking reagent is removed The effect generally takes place in compounds containing π electrons As a result of this effect, bond fission takes place – triple bond being converted into a double bond and a double bond into a single bond Since in this effect complete migration of electron takes place, the atom or group at which the electron has migrated develops the uninegative charge i e I^- and the atom or group from which the electron has shifted develops the unipositive charge i e I^+ Like the inductive effect, the electromeric effect can also be positive and negative and indicated by +E and –E A carved arrow ($\curvearrowright$) starting from the less electronegative atom and ending at the more electronegative atom represents the electromeric effect

When the I and E effect occur together in a molecule, they may be assisting or opposing each other. When they are opposing, the E effect generally dominates over I effect
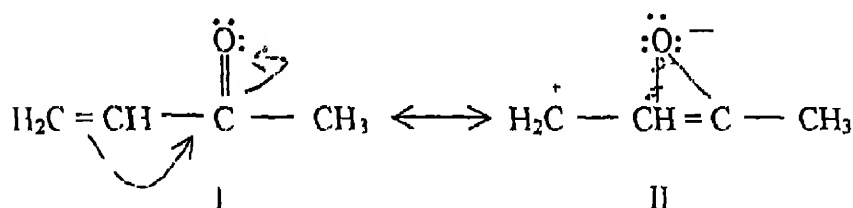
6.3 Resonance or mesomeric effect

Resonance or mesomeric effect helps in understanding the true structure of many such compounds, which cannot be represented, by any single structure on paper Resonance involves overlap of P orbitals both the directions and there is participation of each p electron in more than one bond In other words, resonance involve delocalisation of π electrons The phenomenon of resonance can be best in explained by citing the examples of CO_2 and benzene molecules CO_2 cannot be represented by any single structure It is said to be a resonance hybrid of many structures. It may also be remembered that a double headed arrow represents resonance In resonance, there is no change in overall charge in the molecule though the position of charge may change Resonance leads to stability i e

why it is said that more the resonance, more the stability   Various resonance hybrid structures or canonical forms of CO_2 and benzene are given below

$$:\overset{..}{O} = C = \overset{..}{O}: \longleftrightarrow \overset{+}{}\overset{..}{O} \equiv \overset{-}{C} — \overset{-}{\underset{..}{O}}: \longleftrightarrow :O - C \equiv \overset{+}{O}:$$

I   II   III

IV   V

None of the structures of CO_2 or benzene shown above explains all the properties but each structures is said to be a contributing structure to account for some of the properties   It may also be remembered that in resonance, position of the atom never changes   It is the electron, which changes its position

Resonance or mesomeric effect is represented by R or M   When groups such as $>C = O$, $-NO_2$, $-C \equiv N$, $-COOR$ etc are situated at adjacent positions to multiple bonds, they withdraw electrons from the multiple bonds, through R or M effect and are said to possess $-R$ or $-M$ effect as shown below

$$H_2C = CH — \overset{\overset{..}{O}:}{\underset{|}{C}} — CH_3 \longleftrightarrow H_2C — \overset{\overset{..}{:O:^-}}{CH} = C — CH_3$$

I   II

Similarly, groups such as $-\overline{O}H$, $-\overline{O}CH_3$, $\overline{N}H_2$, Cl, HSO_4^-, $-OH$, $-OR$, $-NH_2$, $-NHR$ etc which can release or donate electrons through resonance or mesomerism are said to posses $+R$ or $+M$ effect or electron releasing resonance effect as illustrated by the following example of venyl chloride accounting for its more stability due to resonance

$$CH_2 = CH - \overset{..}{\underset{..}{Cl}}: \longleftrightarrow H_2\overset{\ominus}{C} - CH = \overset{\oplus}{\underset{..}{Cl}}$$

I   II
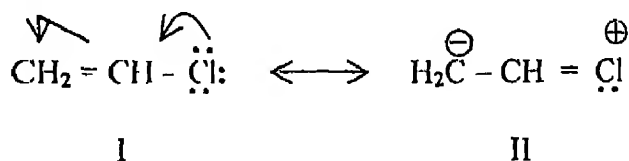
Both resonance and inductive effects are permanent but there are significant differences between the two, which may be highlighted to the students. Resonance effect operates only in unsaturated (preferably one with the conjugated system) compounds but inductive effect operates in compounds containing only sigma (σ) bonds. In other words pi (π) electrons are involved in resonance but only sigma (σ) electrons are involved in inductive effect

Inductive effect is distance dependent (its intensity decreases sharply with distance from the source of electron in the carbon chain) but resonance effect is not   Moreover, resonance involves delocalisation of electrons but in inductive effect there is no such delocalisation
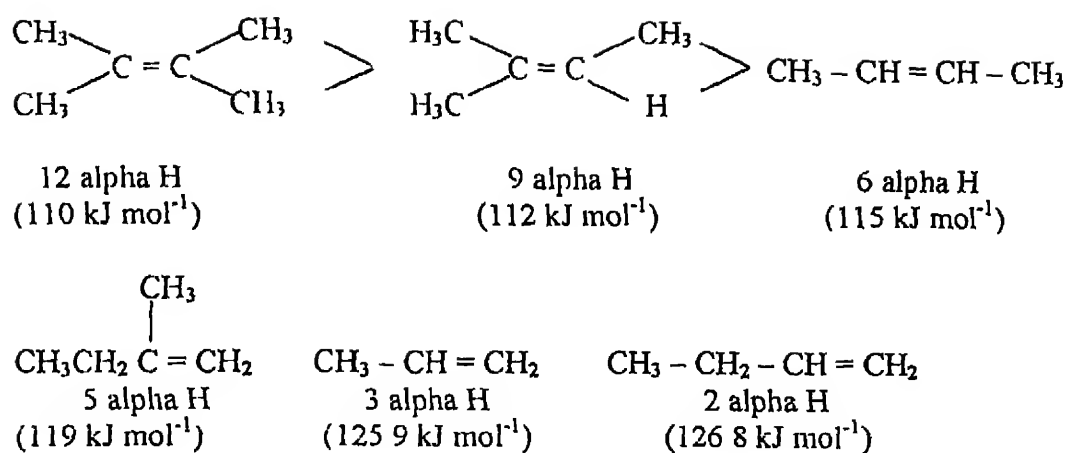
6.4   Hyperconjugation

Conjugated dienes like 1, 3 – butadinene are found to be more stable than simple monoencs like 1-butene due to delocalisation of π electrons Besides conjugations, the alkyl groups bearing H atoms on the alpha carbon to the doubly bonded carbon atoms tend to increase the stability of alkenes i e why propene is found to be more stable than ethene by about 11 kJ mol^{-1} This is due to delocalisation of electrons taking place by the overlapping between pi (π) orbital of carbon and sigma (σ) orbital of the alpha H atoms of the methyl group *The delocalisation of σ bond orbitals with π orbitals is known as Hyperconjugation More the number of hydrogen atoms attached to the alpha carbon bonded to the doubly or triply bonded carbon atoms greater is the Hyperconjugation and greater is the stability.* This can be explained by taking the example of propene in which structure I gets converted into structure II, III and IV due to Hyperconjugation
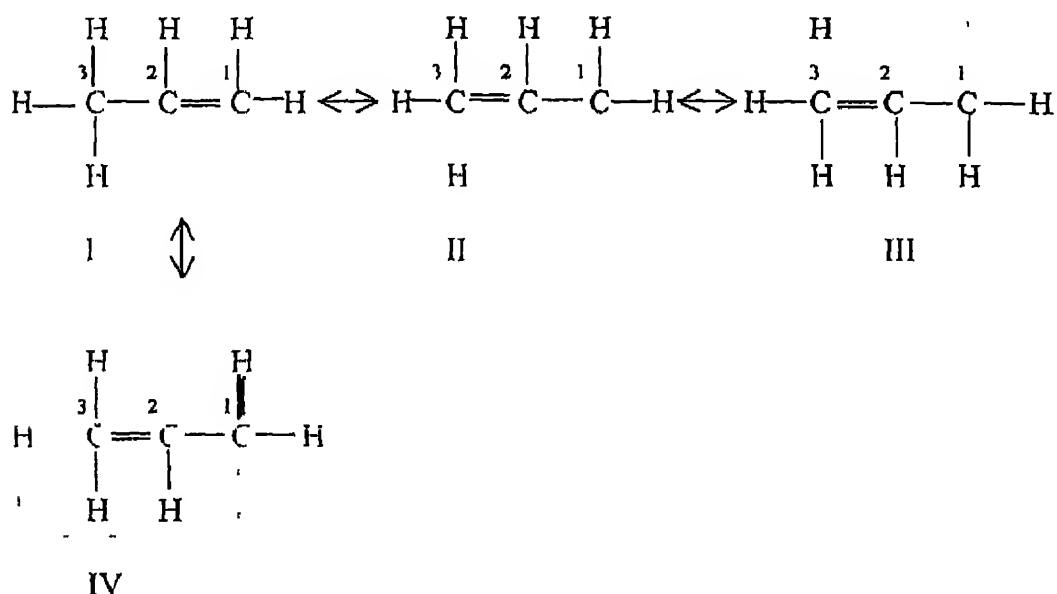
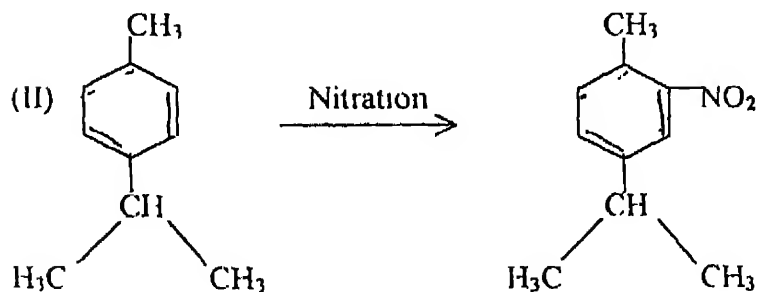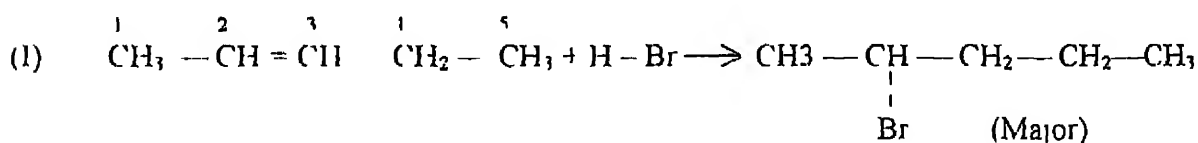Thus propene can be regarded as a resonance hybrid of the above four structures Structures II, III and IV are unusual as they have no real bond joining the hydrogen to carbon These structures are also known as no bond structures $C_2 - C_3$ bond has a slight double bond character as supported by the bond length data when $C_2 - C_3$ bond length has been found of the order of 148 pm and not 154 pm as expected for a pure single bond Structures II, III and IV are having one less real bond then structure I i e due to hyperconjugation, structure I has sacrificed one bond i e why hyperconjugation is sometimes, also termed as sacrificial hyperconjugation

If hyperconjugation effect and inductive effect are operating simultaneously in a molecule then hyperconjugation is found to dominate Hyperconjugation explains the pattern of stability of different alkenes, free radicals and carbocations and predict the formation of the product in electrophilic addition as well as substitution reactions

The substituted alkenes are found to follow the following pattern of stability due to hyperconjugation further supported by their heat of hydrogenation data given in parentheses

$$CH_3\!\!\diagdown\!\!{}_{CH_3}\!\!\!C = C\!\!\diagup^{CH_3}\!\!\diagdown_{CH_3} \quad > \quad H_3C\!\!\diagdown\!\!{}_{H_3C}\!\!\!C = C\!\!\diagup^{CH_3}\!\!\diagdown_{H} \quad > \quad CH_3 - CH = CH - CH_3$$

12 alpha H	9 alpha H	6 alpha H
(110 kJ mol^{-1})	(112 kJ mol^{-1})	(115 kJ mol^{-1})

$$\underset{CH_3}{\overset{\overset{\displaystyle CH_3}{|}}{CH_3CH_2\,C = CH_2}} \qquad CH_3 - CH = CH_2 \qquad CH_3 - CH_2 - CH = CH_2$$

5 alpha H	3 alpha H	2 alpha H
(119 kJ mol^{-1})	(125 9 kJ mol^{-1})	(126 8 kJ mol^{-1})

Similarly out of toluene, ethyl benzene, isprophy benzene and tert butyl benzene, toluene is found to be the most reactive towards electrophilic substitution reactions Here hyperconjugation dominates over the +1 effect of the alkyl group Similarly 2 – pentene on addition with HBr is found to give 2-Bromo pentane as the major product and not 3-Bromopentane due to dominance of hyperconjugation over the inductive effect Similarly, nitration of p – isopropyl toluene will give a product in which the nitro group enters ortho position to the methyl group and not ortho to the isopropyl group though the isopropyl group is found to exert stronger inductive effect than the methyl group again confirming the statement that hyperconjugation dominates over inductive effect. The above reactions can be depicted as given below

(1) $\overset{1}{CH_3} - \overset{2}{CH} = \overset{3}{CH} \quad \overset{4}{CH_2} - \overset{5}{CH_3} + H - Br \longrightarrow CH3 - \underset{\underset{Br}{|}}{CH} - CH_2 - CH_2 - CH_3$ (Major)

(II)

Similarly inductive effect, electromeric effect and mesomeric effects play important role in determining the course of many reactions and in prediction the acidic or basic nature of different molecules While discussing these electronic effects a few simple examples of their applications must be discussed to appreciate their importance in learning of organic chemistry Detailed applications may be taken up latter on while discussing the relevant concepts

It is hoped that learning of the basic principle of organic chemistry will help the students in accelerating their pace of learning besides inculcating reasoning and developing in them the scientific attitude. Hydrogen bonding dipole moment structure size and shapes of molecules will further come to the rescue of the learners in seeking solution to many problems but these have been purposefully left uncovered as these aspects will be taken care of at other places

The following problems may be taken as a brain storming exercise by the teachers as well as the learners

EXERCISE

1) Arrange HCOOH, CH_3COOH and C_6H_5 COOH in decreasing order of their acidic strength

2) Out of CH_3COOH, $CH_2ClCOOH$, CCl_3 COOH and $CHCl_2$ COOH what acid has the lowest pH and why?

3) Arrange CH_2F COOH, CH_2I COOH, CH_2Cl COOH and CH_3 COOH in increasing order of their Pka values

4) Out of NH_3, CH_3NH_2, $(CH_3)_2$ NH, $(CH_3)_3$ N and $C_6H_5H_2$ which has the highest pkb value and why?

5) Arrange CH_2Cl CH_2 CH_2 COOH, CH_3 CH Cl CH_2 COOH and CH_3 CH_2 CH Cl COOH in increasing order of their Ka values

6) Both benzyl alcohol and phenol contain – OH group but aqueous phenolic solution turns blue litmus paper red but benzyl alcohol does not?

7) Vinyl alcohol acidic is nature but allyl alcohol is neutral Why?

8) How do you account for all the six equivalent C – C bond length in benzene when it is said to contain three double bonds and three single bonds?

9) Why is 1 3 – Butadiene more stable than 1 – Butene?

10) Predict the major product of formation as a result of reaction of HBr with - pentane Also give reasons in support of your answer

SOLID STATE

Prof. G.T Bhandage

2.1 **Introduction :** The advancement in Science and Technology of solids is essentially due to the awareness that structure and properties are related at the molecular level The correlations between Chemical bonding, structure, imperfections and properties are shown below
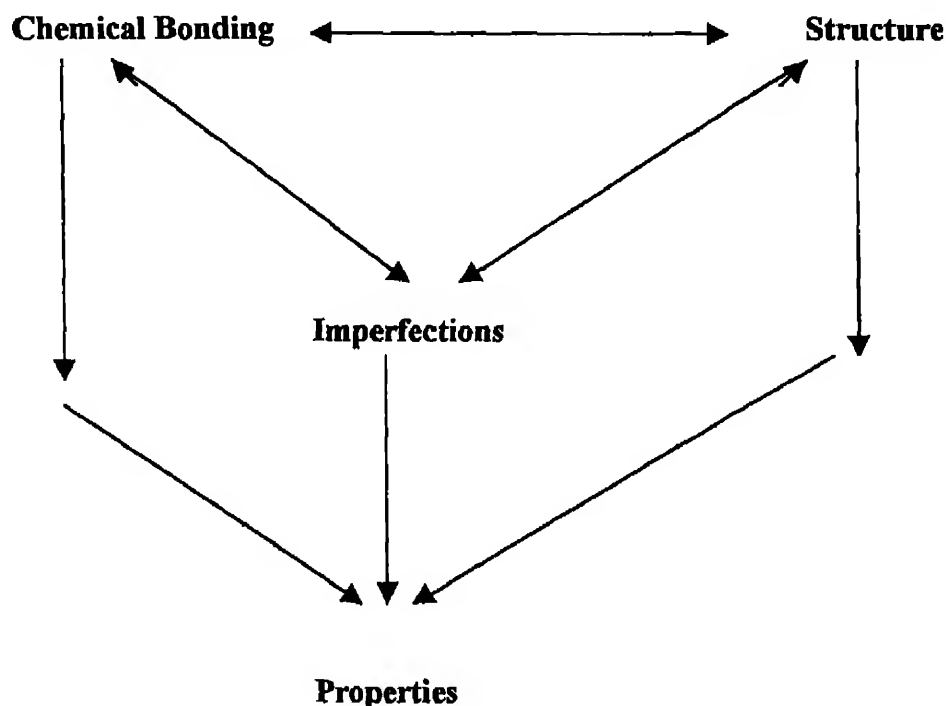
Today the science and technology of materials is in such an advanced state as to allow the application of physico-chemical principles for the design of newer materials in ceramic single crystals and or amorphous forms Semiconductors, ferrites, magnetic garnets, solid state lasers, piezoelectric, ferroelectrics, ultraviolet and IR sensitive crystals and of late superconductors etc are some of the solid devices which have revolutionized modern-day technology (Fig. 2.1)

Solids are generally classified into crystalline and amorphous Crystalline solids are considered as true solids in which atoms, molecules or ions are held together by strong forces giving repetitive three dimensional arrangements. They are characterized by well-defined planes, angles,with sharp melting points, characteristic heats of fusion etc On the
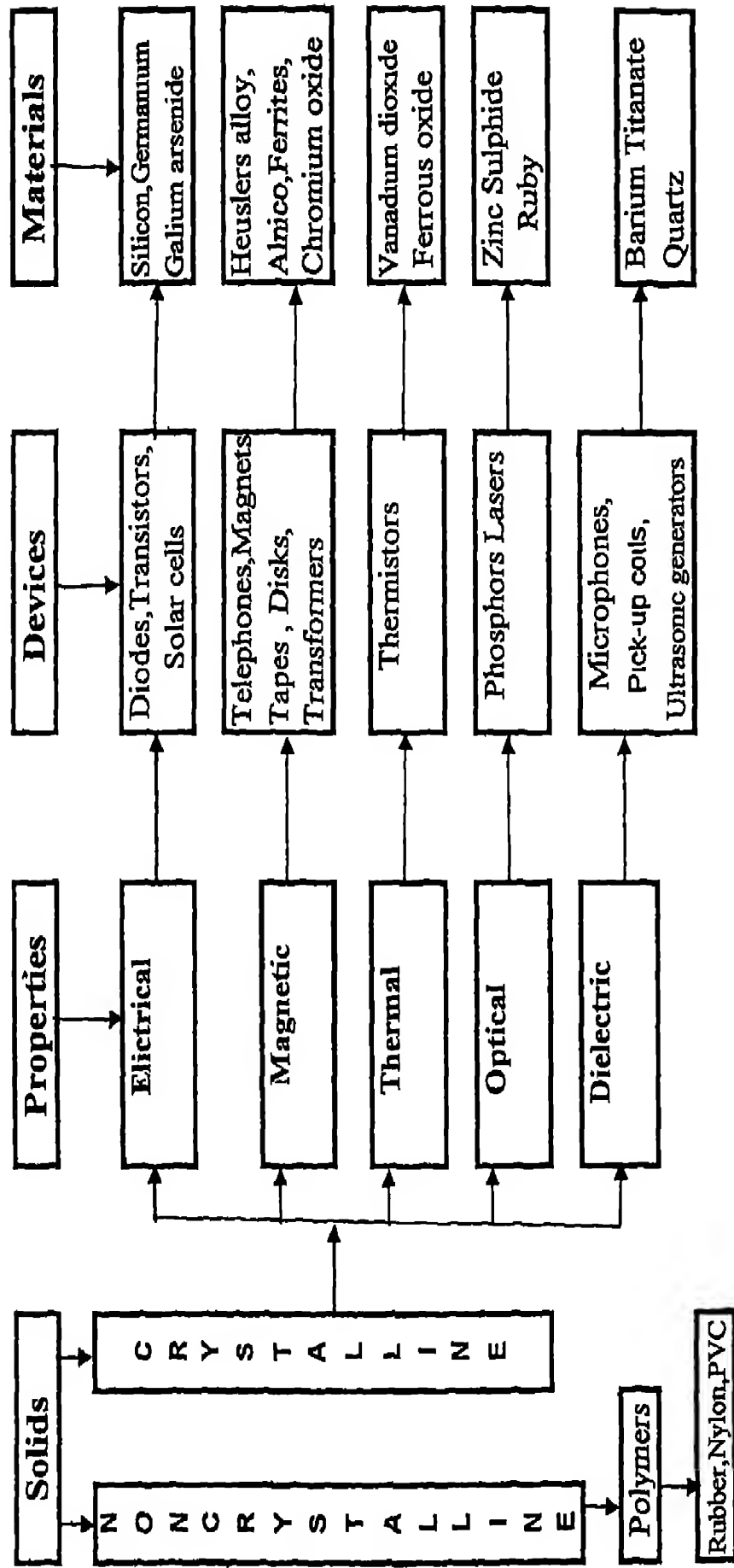
Material Properties & Devices

Properties	Devices	Materials
Electrical	Diodes, Transistors, Solar cells	Silicon, Germanium Galium arsenide
Magnetic	Telephones, Magnets Tapes, Disks, Transformers	Heuslers alloy, Alnico, Ferrites, Chromium oxide
Thermal	Thermistors	Vanadium dioxide Ferrous oxide
Optical	Phosphors Lasers	Zinc Sulphide Ruby
Dielectric	Microphones, Pick-up coils, Ultrasonic generators	Barium Titanate Quartz

Solids

CRYSTALLINE

NON CRYSTALLINE

Polymers

Rubber, Nylon, PVC

Fig 2.1

other hand amorphous materials or pseudo solids are formed by random, nonrepetitive three dimensional arrangement as exemplified by glass, rubber, polymers etc.

2.2 Classification based on binding forces:

| Crystal type	Constituent particles	Major binding forces	Properties	Examples
Molecular	Small molecules	Van der Waal forces	Soft, low m.p., volatile,electrical insulators, poor thermal conductors, low heats of fusion	Solid CO_2, iodine, ice, sulphur
Ionic	Ions arranged systematically	Strong electrostatic interactions	Brittle, high m.p., poor conductors of electricity,heat high heats of fusion	NaCl, LiF, $BaSO_4$
Covalent	A network of chemically bound atoms of one or more kinds	Covalent forces	Very hard, high m.p., poor conductors of heat, high heats of fusion	Diamond, silicon, quartz
Metallic	Positive ions in a sea of electrons	Electrical attraction	Very soft to hard, low to high m.p., conductors of heat, electricity, metallic lustre etc.	Common metals and some alloys

The Unit Cell
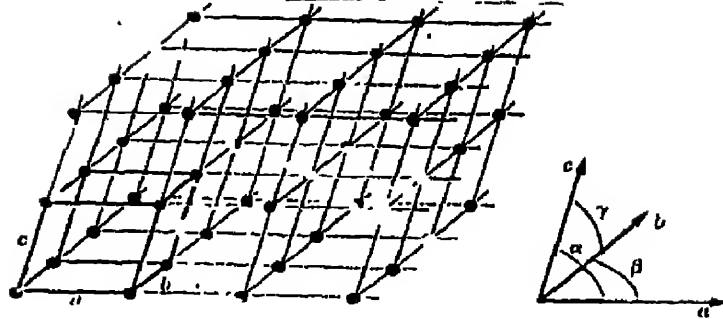
Fig. 2-2 A lattice of points, showing the unit cell in heavy outline, and three fundamental translational vectors, a, b, and c.
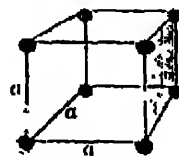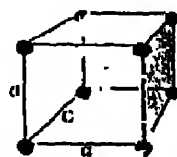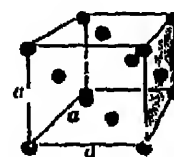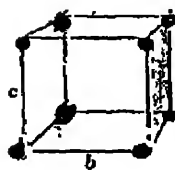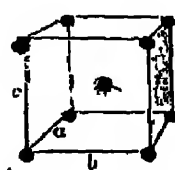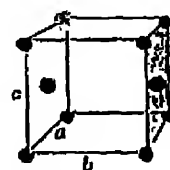

Simple   Body-centered   Face-centered

CUBIC

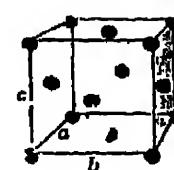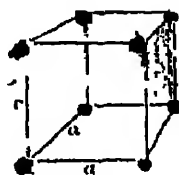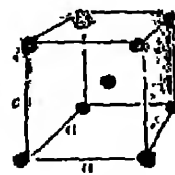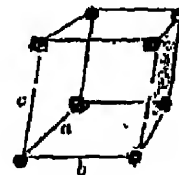Simple   Body-centered   End-centered   Face-centered

ORTHORHOMBIC
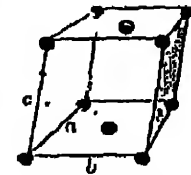
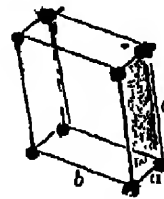Simple   Body-centered   Simple   End-centered
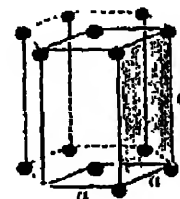
TETRAGONAL   MONOCLINIC

Rhombohedral   Triclinic   Hexagonal

Unit cells of the 14 Bravais Lattices grouped into the seven crystal system

BRAVAIS LATTICES

2.3 Crystal lattice: The infinite repetition of orderly arrangement of particles in crystal, means if we start at one atom and travel along specific direction we must arrive at another atom with identical environment A representation of points in space (Fig. 2 2) is space lattice. Three dimensional group of points (point of space lattice) is called **Unit Cell.** It is characterised by definite edges-a,b,c and angles-α,β and γ The whole crystal is developed by repetition of unit cell in all three dimensions

In all there are seven basic or **primitive unit cells** recognised as 7 crystal systems They are presented in the following table 2 1 Simple cubic lattice has atoms only at the corners,FCC has at faces in addition to corners while BCC has an atom or ion at the centre of the body of the lattice in addition to corner During the growth of crystals, the sizes and shapes may vary for a given material but angles between faces are always the same i e they have the same unit cell

All the known crystals can be classified into seven crystal systems, which in turn belong to fourteen Bravais lattices as shown below

2.4 Close-packed structures :

The regularity of packing in solids arises from geometrical constraints which are imposed mainly by directional bonding and close packing A close-packing is a way of arranging identical objects in space so that the available space is filled very efficiently. Such an arrangement is achieved when each object is in actual contact with the maximum number of like objects. Using available space in the most economic way is inherent in the nature Interestingly bees form hexagonal cells to store their honey in order to utilise the space most efficiently.

Condensation in solids is the result of some kind of attractive force operating between constituent atoms, ions or molecules As a first approximation, atoms may be considered as hard spheres packed in such a way that energy is minimum in closest packing and that the spheres have maximum number of neighbours. Almost all metals crystallise in close-packed structures

2.5 Voids in closest packing: The type and size of voids play an important role in building **crystal structures of compounds.** Frequently the larger kind of atoms/ions present in a crystal are in closest packing while smaller atoms/ions occupy the voids between the closest-packed atoms/ions

Table 2.1: Different Crystal Systems

System	Axial distances.	Axial angles	Examples
Cubic	$a=b=c$	$\alpha=\beta=\gamma=90°$	Copper, Zinc blende, KCl
Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90°$	White tin, SnO_2
Orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90°$	Rhombic sulphur
Monoclinic	$a\neq b\neq c$	$\alpha=\gamma=90°; \beta\neq90°$	Monoclinic sulphur
Hexagonal	$a=b\neq c$	$\alpha=\beta=90°; \gamma=120°$	Graphite
Rhombohedral	$a=b=c$	$\alpha=\beta=\gamma\neq90°$	Calcite
Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq90°$	Potassium dichromate

Metals and Non-Metals in the Periodic table
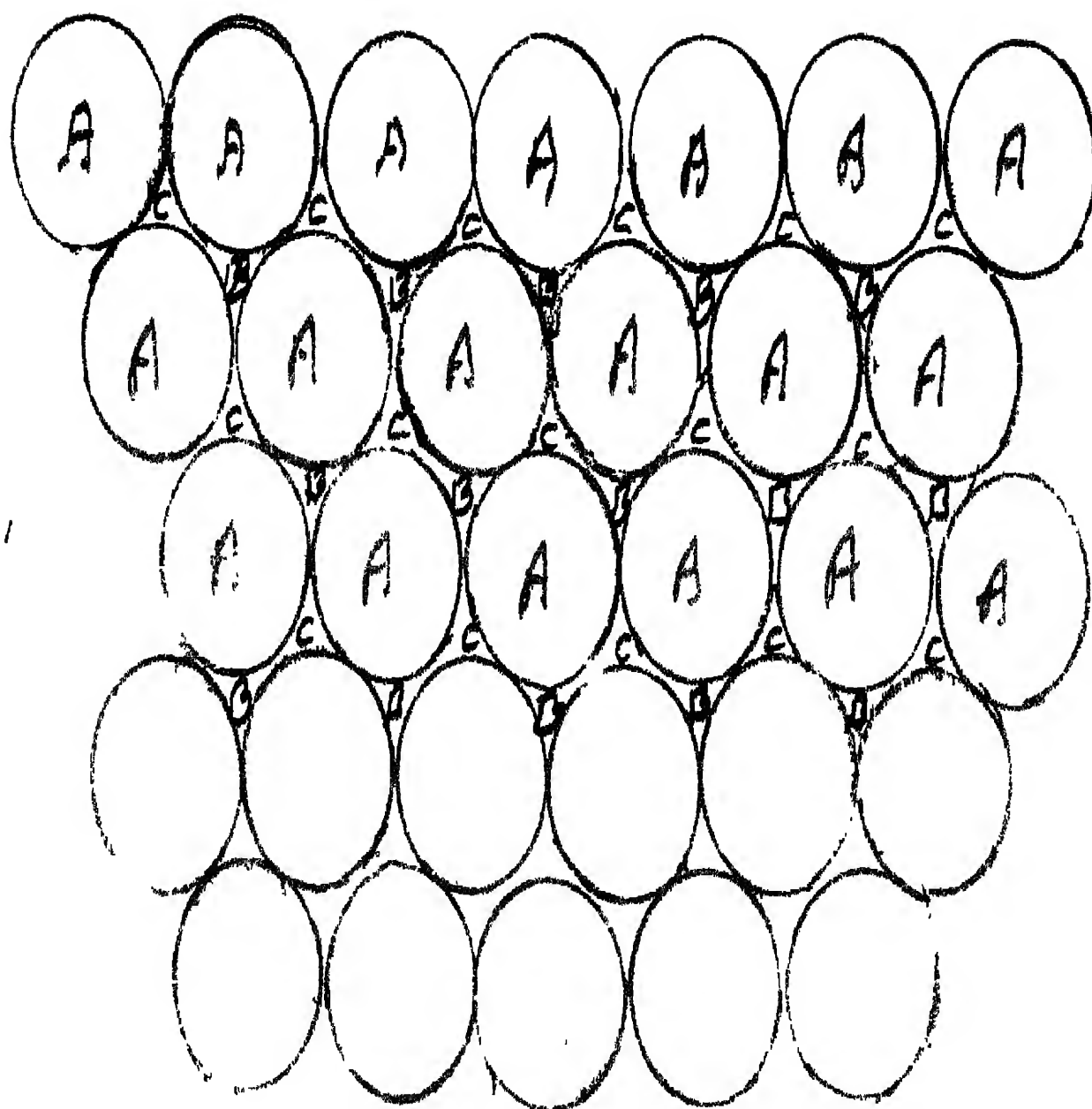

21
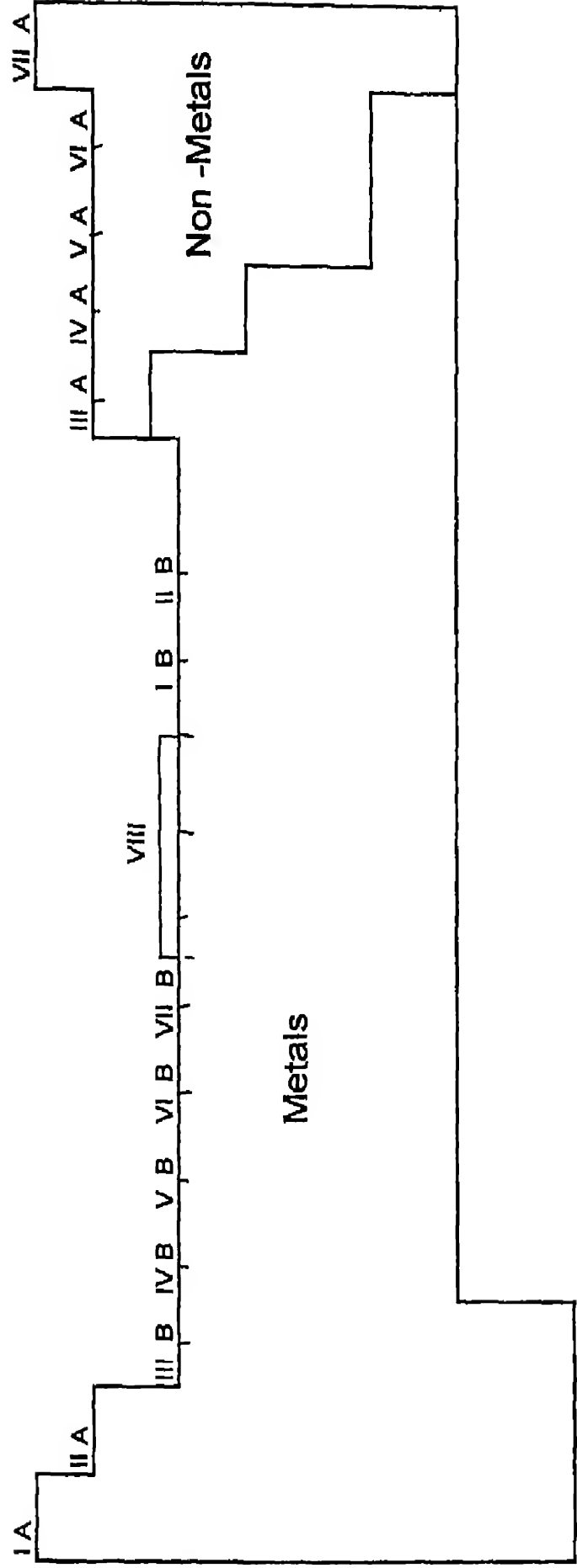
Fig 2.2

There are two kinds of voids that occur in all closest packings. If a triangular void has a sphere over it, there results a void with four spheres around it-called **tetrahedral void.** For such a void, four spheres are arranged in the corners of a regular tetrahedron If a triangular void pointing up in one close-packed layer is covered by triangular void pointing down in an adjacent layer, then a void surrounded by six spheres results. These six spheres are arranged at the corners of a regular octahedron and such a void is called an **octahedral void** (Figs 2.2 to 2.4).

The closest-packed layer above the A layer gives rise to three tetrahedral and three octahedral voids. Similarly, the closest-packed layer below the A layer also gives three tetrahedral and three octahedral voids. Further, the particular sphere being considered in layer A itself covers a triangular void each in close-packed layers above and below it. This results in 2x3=6 octahedral and 2x3 +1+1=8 tetrahedral voids surrounding the sphere. Each octahedral void is surrounded by six spheres and each sphere is surrounded by six octahedral voids. Thus the number of octahedral voids belonging to one sphere is 1 Similarly each tetrahedral void is surrounded by four spheres and each sphere is surrounded by eight voids. Thus the number of tetrahedral voids belonging to one sphere is 2

2.6 Packing and radius-ratio rule: Ionic solids offer best examples of packing determined by the relative sizes of ions because anions and cations usually differ in size. The possible values of coordination (ligancy) in a 3-dimensional regular array of ions are 2,3,4,6,8 and 12.

The range of radius ratio $r+/r$. over which each value of coordination number becomes stable can be predicted provided the following conditions are believed to be satisfied: a) The cations and anions are at their inter-ionic positions. b) The anions do not overlap with each other (their centres do not approach more closely than the ionic diameter.). c) Each cation tends to be surrounded by the largest possible number of anions, as the difference between ionic sizes become smaller, higher values of coordination number can occur.

Sphere in Cubic Hole

$\sqrt{C}$ = Radius of Cation

$\sqrt{A}$ = Radius of anion

$2\sqrt{2}\sqrt{A}$

$2(\sqrt{A}+\sqrt{C})$
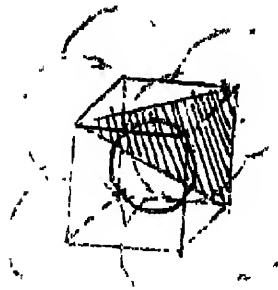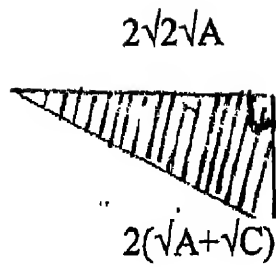
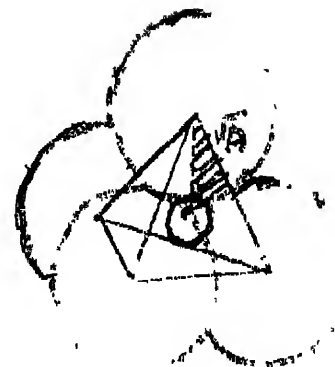$$[2(\sqrt{A}+\sqrt{C})]^2 = (2\sqrt{A})^2 + [2\sqrt{2}\sqrt{A}]^2$$

$$2(\sqrt{A}+\sqrt{C}) = 12\sqrt{A}^2 = \sqrt{12}\sqrt{A}$$
$$\sqrt{C}/\sqrt{A} = 0.732$$

Sphere in Tetrahedral Hole

$\sqrt{A}+\sqrt{C}$

$\sqrt{A}$

$\theta = 54\ 3/4°$

$$\text{Sin } 54\ 3/4° = 0.817 = \frac{\sqrt{A}}{\sqrt{A}+\sqrt{C}}$$

$$\therefore 0.817\sqrt{C} = 0.183\sqrt{A}$$

$$\sqrt{C}/\sqrt{A} = 0.225$$

Fig.2.3

24

Sphere in Octahedral Hole
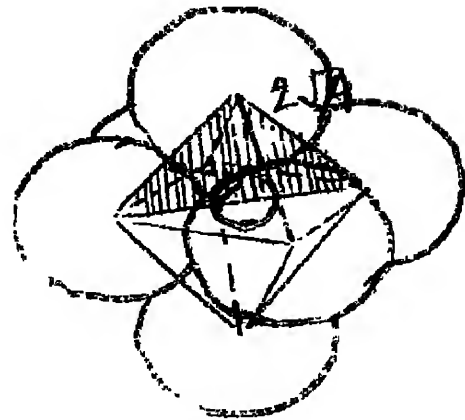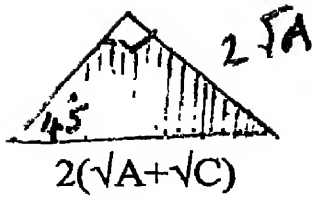
$$\text{Sin } 45^\circ = 0.707 = \frac{2\sqrt{A}}{2(\sqrt{A}+\sqrt{C})}$$

$$\therefore \quad \sqrt{C} / \sqrt{A} = 0.414$$

Sphere in Triangular Hole
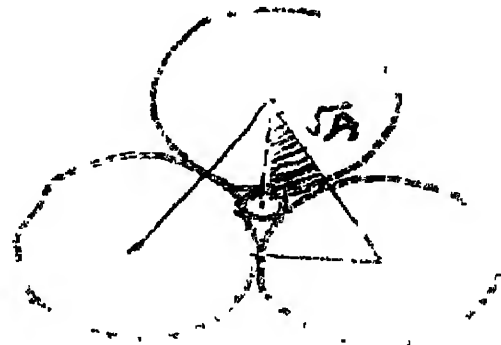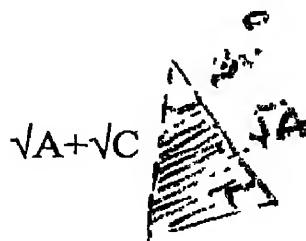
$$\sqrt{A} \quad / \sqrt{A}+\sqrt{C} = \text{Cos } 30^\circ = 0.866$$

$$\sqrt{A} = 0.866 \, (\sqrt{A}+\sqrt{C})$$

$$0.866 \, \sqrt{C} = (1- 0.866) \, \sqrt{A}$$

$$\sqrt{C} / \sqrt{A} = 0.155$$

Fig.2.4

	Packing (shape)	Coordination number
0.0-0.155	Linear	2
0.155-0.225	Triangle(corners of equilateral triangle)	3
0.225-0.414	Tetrahedral(corners of tetrahedron)	4
o.414-o.732	Octahedron(corners of octahedron or square)	6 or 4
0.732-1.0	Cubic (corners of a cube)	8
1.0	HCP	12
1.0	FCC	12

A Few Concerns in Sterochemistry

Dr. V.P. Gupta

Chapter on stereochemistry has been introduced by NCERT in class XII text book of chemistry with effect from 2003. Though there was some mention of geometrical and optical isomerism in earlier chemistry syllabus at senior secondary level but many new concepts like Z and E configuration of geometrical isomers, R and S and D and L configurations for chiral and compounds, conformation of higher alkanes and cycloalkanes like butane and cyclohaxane have been introduced in the new curriculum. Interaction with students and Chemistry PGTs of Navodaya Vidyalayas and that of Demonstration schools and Kendriya vidyalaya has also revealed the need for discussion on different aspects of the newly introduced topic. Following are some of the concerns / hard spots which should be clarified by the teachers very intensively while discussing this topic in class XII

1. Concept of stereochemistry
2. Conformations
3. Cis , trans; syn anti geometrical isomers
4. CIP Rules for Z and E and R and S configuration
5. Z and E configuration of geometrical Isomers
6. Chirality of molecule
7. R and S Configuration of Chiral molecules
8. D and L Configuration of Chiral molecules
9. Condition for Optical Activity
10. Enantiomerism and diastereomerism
11. Resolution

A brief discussion on each of the above is given below with the view to bring more clarity on the subject matter and to make this topic more interesting and meaningful

1. Stereochemistry

Stereochemistry is that branch of chemistry which deals with the study of spatial arrangement of different atoms or groups of the molecule i.e. how different

atoms or groups of atoms in a molecule are arranged with respect to one another in three dimensional space.

Difference in spatial arrangement of atoms or groups in a molecule gives rise to different isomers differing in their properties Such isomers are known as stereo or space isomers. Stereoisomers possess the same molecular formula and similar structure i.e. the same sequence of covalent bonds but relative position of atoms or groups in space is different For example, each of us has two hands and two legs but spatial arrangement of two hands or legs makes each of them a specific left hand or left leg or right hand or right leg with respect to our body.

Stereoisomers can be divided into two categories namely conformations and configurational isomers. **Conformations are the different spatial arrangements of atoms or group of atoms obtained by free rotation of C–C sigma bonds (without breaking and forming of covalent bonds). Configurations, on the other hand, are those space isomers, which exist due to certain rigidity within the molecule, Hence, they can be inter-converted only by breaking and setting up of new bonds.** They can be of two types – namely (i) Geometrical and (ii) optical isomers A brief description of each is given below

2. Conformations

As already stated that conformations are different spatial arrangements of different atoms or groups obtained by rotation of C – C sigma bond keeping one carbon atom in a fixed position. Let's consider ethane molecule, which consists of two carbon atoms Each carbon atom is attached to three hydrogen atoms If any one-methyl group is kept fixed, position of hydrogen atoms attached to the other carbon atom can be changed w r t hydrogen atoms attached to first carbon atom by rotating around the single covalent C – C bond. One possibility will be in which each hydrogen atom of C_1 lies over each hydrogen atom of C_2 Such a spatial arrangement is called eclipsed conformation since hydrogen atoms of one carbon atom have eclipsed the hydrogen atoms of the ether carbon atom. Teachers can make students understand that in such a situation there is more crowding of atoms as they are very close to each other It will be difficult to keep hydrogen atoms together due to Vander Waals repulsion between them Thus it can be concluded that the eclipsed spatial arrangement is associated with more energy and hence

more unstable The other extreme spatial arrangement will be in which the two hydrogen atoms (say H_1 of C_1 and H_2 of C_2) which were lying one above the other in eclipsed from get – separated by a bond angle of $180°$ i e. the $C - C$ single bond is given a rotation of $180°$ Such a form is called staggered conformation Since in this form the hydrogen atoms are farthest apart from each other, there is least crowding and hence this form is associated with least energy. Such a form of least crowding and least energy is known as staggered conformation. Between these two extreme conformations there will be infinite number of conformations differing in relative position of hydrogen atoms with respect to each other **Eclipsed, staggered and various other conformations of ethane can be demonstrated by the teacher with the help of balls and stick model keeping position of one carbon atom fixed and changing position of the carbon atom.**

2.1 Conformations of Propane and Butane

Similarly conformations of propane and butane can be demonstrated by keeping position of C_2 fixed and rotating C_3 around the single covalent bond between C_2 and C_3 Newmen projections of ethane, propane and butane have been shown in NCERT textbook (class XI p 310,311) very effectively representing the carbon atom towards us by C· black point and C_2 away from us by a black circle. Hydrogen atoms attached to C_1 are shown by black single covalent bonds and hydrogen atoms attached to C_2 away from us by blue dotted lines The concept of eclipsed and staggered conformations can be better clarified by representing hydrogen atoms attached to C_1 as H_1, H_2 and H_3 and hydrogen atoms attached to C_2 as H_1^1 H_2^1 and H_3^1 .Students will now appreciate the difference between eclipsed and staggered conformations when they find that H_1 and H_1^1 lying one above the other in eclipsed form get farthest apart (opposite to each other obtained by rotation of $180°$) in the staggered form which otherwise becomes a bit difficult, if all the hydrogen atoms are represented as H as given in most of the books

2.1   Conformations of Cyclohexane

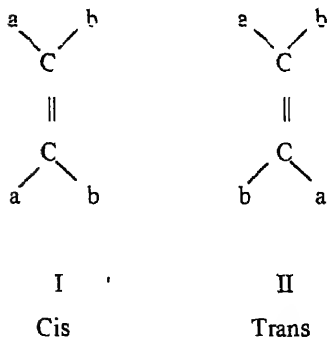According to Baeyer strain theory, cyclohexane molecule is assumed to be a planar molecule with $C - C - C$ bond angle of $120°$. Later on it was proved by Herman Sachse and Mohr that cyclohexane molecule is not planar rather it gets puckered due to which the molecule tends to take the shape of a chair and a boat with the $C - C - C$ bond angle very close to the tetrahedral bond angle The puckering (slight twisting)

phenomenon of cyclohoxane molecule can again be demonstrated with the help of balls and sticks model. The staggered form is stabler than eclipsed form model of cyclohexane. If the staggered conformation is stabler than the eclipsed form by 12.8 kJ mol^{-1}, the chair form of cyclohexane is stabler than the boat form by 28 kJ mol^{-1}

This is because of the fact that all the carbon carbon bonds and carbon hydrogen bonds in chair form are perfectly staggered bonds whereas they are eclipsed in the boat form. Moreover, there is repulsion between the flagpole axial hydrogen atoms attached to C_1 and C_4 in boat form causing instability to that form. The carbon – carbon atoms of chair form of cyclohexane lie in a plane Each C atom is attached to two hydrogen atoms The hydrogen atoms lying in the plane of the ring are called equatorial hydrogen atoms and the other six hydrogen atoms lying below or above the plane of conformations of cyclohexane (axial) can be drawn by giving slight twisting to different bonds Half chair and twist are some other conformations of cyclohaxane.

3. Cis , Trans and Syn and Ante Geometrical Isomerism

When two different atoms or groups are attached to the doubly bonded carbon atom i.e molecules of the type bac = cab can be represented in space in two forms—I & II

I '   II
Cis   Trans

These two forms are not inter-convertible as rotation of atoms around the doubly bonded carbon atoms is not possible The form I and II are known as cis and trans form respectively. This point of restricted rotation around C= C bond can be understood with the help of a ball and stick model or by taking two card board sheets and joining them by two nails when it will be observed that the card sheets cannot be rotated. It may be emphasized by the teachers that the two atoms or groups attached to C atom atoms should be different If two different atoms or groups are attached to one carbon and two same

atoms or groups are attached to the other carbon then two different stereoisomers will not be possible i.e. there will be one and only one spatial representation for abc = caa or bbc = cab The following exercise may be useful to understand the concept of cis – trans isomerism in a better way:

1. **Which of the following will not show geometrical isomerism ?**

   a. $CH_3 - CH = C\ (CH_3)\ C_2H_5$
   b. $C_2H_5 - CH = CH\ C_2H_5$
   c. $C_2H_5 - CH = C\ (CH_3)_2$
   d. $CHCl = CHCl$

2. **Write cis and trans isomers of the following:**
   a. $CHCOOH = CHCOOH$
   b. $CH_3 - CH = CH - CH_3$
   c. $CH_3\ CH = CH - COOH$
   d. $C_2H_5 - CH = CH - COOH$
   e. $CH_3\ (CH_2)_7\ CH = CH - (CH_2)_7 - COOH$
   f. $C_2H_5 - CH = CH - C_2H_5$

Trans isomer is found to be more stable due to symmetry of the molecule since the identical groups (small or big) lying across the double bond tend to balance the molecle, which result in better packing of the crystal lattice. Hence, it can be predicted that the trans isomer will have higher m p than the cis isomer and it is found to be true In case of liquids, the cis isomer is found to have higher boiling point than the trans one It is also observed that the cis isomer has higher dipole moment than the trans isomer Answers of these problems are not given here purposefully. Such types of problems may be raised by the teachers in the class and let the students find answers to these problems Similarly, it can also be explained that due to spatial disposition of different groups in space around the double bond that maleic acid (cis form) forms anhydride on heating but fumaric acid (trans form) does not form fumaric anhydride.

Cyclic compounds like decalin are also found to exhibit cis – trans isomerism. What about α - D (+) – Glucose and β - D (+) – Glucose? Please think over and discuss with your colleagues.

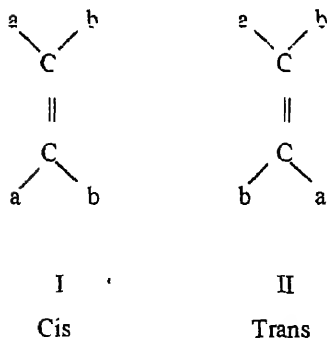Aldoximes are the compounds obtained by nucleophilic substitution of hydroxylamine (NH_2OH) with aldehydes in the presence of dry HCl gas.

phenomenon of cyclohoxane molecule can again be demonstrated with the help of balls and sticks model. The staggered form is stabler than eclipsed form model of cyclohexane. If the staggered conformation is stabler than the eclipsed form by 12 8 kJ mol^{-1}, the chair form of cyclohexane is stabler than the boat form by 28 kJ mol^{-1}

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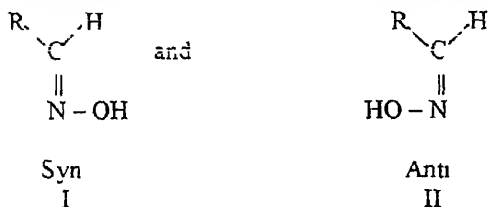   f. $C_2H_5 - CH = CH - C_2H_5$

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Aldoximes are the compounds obtained by nucleophilic substitution of hydroxylamine (NH_2OH) with aldehydes in the presence of dry HCl gas.

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$$R - CH = O + \begin{array}{c} H \\ \diagdown \\ N-O-H \\ \diagup \\ H \end{array} \xrightarrow{\text{dry HCl has.}} \begin{array}{c} RCH = NOH \\ \text{Aldoxime} \end{array}$$

$$\begin{array}{c} CH_3 - C = O + \\ | \\ H \end{array} \begin{array}{c} H \\ \diagdown \\ N-O-H \\ \diagup \\ H \end{array} \xrightarrow{\text{dry HCl gas}} \begin{array}{c} CH_3 - CH = NOH \\ \text{Acetaldoxime} \end{array}$$

$$\begin{array}{c} C_2H_5 - C = O + \\ | \\ H \end{array} \begin{array}{c} H \\ \diagdown \\ N-O-H \\ \diagup \\ H \end{array} \xrightarrow{\text{dry HCl}} \begin{array}{c} C_2H_5 - CH = NOH \\ \text{Propionaldoxime} \end{array}$$

Aldoximes can also be represented in space in the following two ways

$$\begin{array}{c} R \quad\quad H \\ \diagdown \diagup \\ C \\ || \\ N - OH \end{array} \quad \text{and} \quad \begin{array}{c} R \quad\quad H \\ \diagdown \diagup \\ C \\ || \\ HO - N \end{array}$$

Syn	Anti
I	II

(- OH is cis w.r.t H)   (- OH is trans w.r.t.H)

The form I in which –OH group is cis w.r.t. H atom is known as syn aldoxime and the form II in which –OH group is trans w.r.t. H atom is known as anti aldoxime

## 4. CIP Rules for Z-E and R-S configuration

Cahn, Ingold and Prelog (CIP) gave certain rules to decide priority order of groups attached to carbon atom. These rules help in deciding Z-E configuration of geometrical isomers and R and S configuration of Chiral compounds A brief description of the rules is given below·

Sequence Rule – 1

Higher priority is given to the group containing central atom of higher atomic number i e the atom of higher atomic number is given higher priority. Thus out of Cl and Br, Br atom is given higher priority than Cl atom. Similarly out of H, Cl, Br and I, the
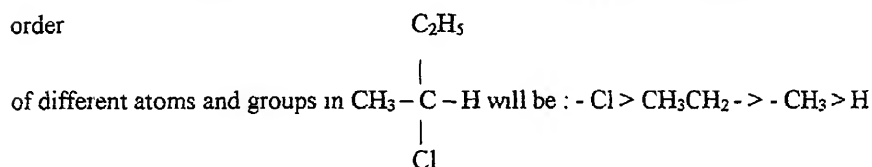
decreasing priority order will be I > Br > Cl > H If isotopes of the same element are present, then isotope of the higher mass number is given priority. Thus out of CH_3, Br, H and D, the priority order will be Br > CH_3 > D > H.

The priority order of different atoms or groups is given below.
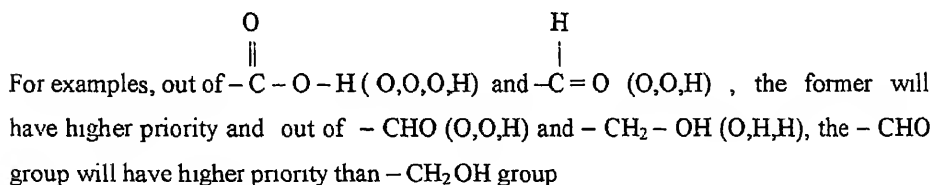
I > Br > Cl > SH > F > -OH > NH_2 > CH_3 > D >H
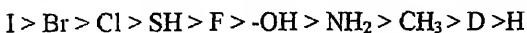
Sequence Rule – 2

If the first element in both the groups happens to be the same then the priority order is decided by priority of the second element. For example, out of - CH_3 group and CH_3 – CH_2 – group, ethyl group gets the priority since in ethyl group, the second element after carbon is again carbon whereas it is H in - CH_3 group For example, the priority order

$$\begin{array}{c} C_2H_5 \\ | \\ \text{of different atoms and groups in } CH_3 - C - H \text{ will be} : - Cl > CH_3CH_2 - > - CH_3 > H \\ | \\ Cl \end{array}$$

Sequence Rule - 3

A doubly or triply bonded atom is equivalent to two or three such atoms, but two or three atoms if actually bonded to another atom will have a priority higher than that of the doubly or triply bonded atom.

$$\begin{array}{cc} O & H \\ \| & | \end{array}$$

For examples, out of $- C - O - H$ (O,O,O,H) and $-C = O$ (O,O,H) , the former will have higher priority and out of – CHO (O,O,H) and – CH_2 – OH (O,H,H), the – CHO group will have higher priority than – CH_2 OH group
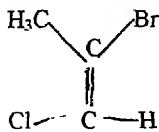
5. Z-E Geometrical Isomers

Letters Z and E are the abbreviation of German words Zusamen (together) and entgegen (opposite) and are used to indicate the configurations of the tri and tetra-substituted alkenes because they cannot be differentiated by prefixes like cis and trans For assigning Z and E configuration to such substituted alkenes, priority order of the two substituents attached to each of the doubly bonded carbon atoms are decided as per CIP rules discussed earlier. If the atoms or groups of higher priority are on the same side of the double bond i.e, if they are together, the isomer is given Z configuration, otherwise it is known as E.

Let's consider configurations of isomers corresponding to $CH_3 CBr = CHCl$. The four atoms | groups are given the priority order of $Br > Cl > CH_3 > H$. The above compound can be represented in space in the following two ways.
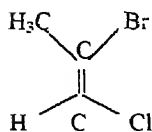
I	II
2–Bromo–1–Chloropropene (Z)	2 – Bromo – 1 – Cholropropene (E)

In isomer I, both the high priority groups Cl_3 and Br are on the same side of the double bond i.e. they are together. Hence I is given Z nomenclature and II the E nomenclature. Z – E nomenclature can be applied to di – substituted alkenes i.e cis – trans geometrical isomerism also The following exercise may be useful for further strengthening of this concept

Assign Z – E nomenclature to isomers of the following compounds:

1. $CH_3 CCl = C\ Cl\ Br$
2. $CH_3 CH = CH\ CH_3$
3. $C_2H_5 - CH = CH - COOH$

6. Chirality of Molecule and Optical Activity

After the concept of tetrahedral Carbon given by Le Bell and Van't Hoff (1874), it was observed that if the four atoms or groups attached to carbon atom were different, then such a molecule Cannot superimpose its mirror image Such a molecule is referred to as the asymmetric or chiral molecule and the carbon atom to which four different atoms or groups are attached is known as asymmetric or chiral carbon atom This can be compared to our left and right hands which are mirror images of each other but they are not superimposable When solution of such a chiral molecule or the substance in its liquid state is placed in a polarimeter tube and plane polarized beam of light is passed through such a solution, the plane polarized beam of light is found to deviate from its original path either towards right or towards left. If the chiral molecule (lactic acid, 2 – Chlorobutane, glucose, fructorse, bromo chloro – iodomethane .) tilts the path of plane polarized beam of light towards right, its mirror image will tilt towards left but to the

same extent if solutions of same concentrations are used. The chiral molecule and its mirror image having similar structure, similar physical and Chemical properties (except the phenomenon of resolution by using chiral reagent) like m.p b p. density refractive index, adsorption, surface tension, viscocity etc are known as optical isomers or enantiomers. **Thus enantiomers may be defined as the stereoisomers, which are mirror images of each other, non – superimposable and differing in their action toward a plane polarized beam of light.** At this stage it may be highlighted that the stereoisomer rotating the path of plane polarized beam of light towards right i.e. in the clockwise direction is known as dextro rotating and is represented by d or (+). The other stereoisomer rotating the path towards left is known as leavo rotating and abbreviated as l or (-). Taking the examples of lactic acid and, 2 – Bromobutane or such molecules and their mirror images and drawing their Fischer's structures may further strengthen this concept It may also be highlighted that the chiral molecule cannot be cut into two identical halves i.e it cannot have a plane of symmetry

7, R and S Configuration to Chiral Molecule

R and S are the abbreviations of latin words Rectus (Right) and Sinister (Left) To assign R or S configuration to the chiral molecule, priority order of all the four atoms or groups is decided with the help of CIP rules as mentioned earlier After deciding priority of the four atoms or groups, the molecule is so visualized that atom group of lowest priority is directed away from us The remaining atoms or groups are now arranged in decreasing order of priority. The Configuration is assigned R Configuration if eye travels in clockwise direction otherwise S configuration is assigned It may be pointed out by the teachers that direction of rotation of an optically active isomer is independent of the R or S configuration This can be explained by taking the example of Bromo, Chloro, iodomethane which can be assigned R and S configuration as given below:

Br
|
H – C – Cl
I

R

Br
|
H – C – I
Cl

S
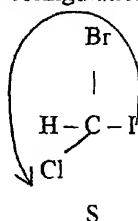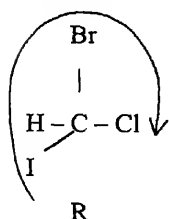
For strengthening of the concept, the following exercise may be useful

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Exercise

Indicate R and S Configuration to Stereoisomers of
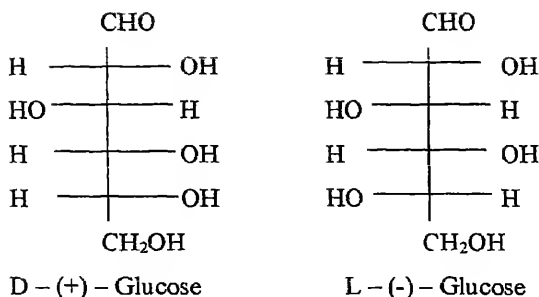
    (i)   2 – Methyl – butan – 1 – ol
    (ii)   Secondary butyl bromide
    (iii)   1 – Bromo – 1 – Chloroethane

---

8. D and L Configuration of Chiral Molecules

    D and L configuration has been another way of representing the absolute configuration of Chiral molecules. This terminology finds its genesis in configuration of glyceraldehyde arbitrarily adopted by Fischer. Fischer used D terminology for that isomer in which –OH group attached to chiral carbon atom in glyceraldehyde lied towards right and L for the other one in which –OH group was on L H.S. D and L forms of glyceraldehyde are represented below

$$
\begin{array}{ccc}
\text{CHO} & & \text{CHO} \\
| & & | \\
\text{H} \rule{1cm}{0.4pt}\!\!\!+\!\!\!\rule{1cm}{0.4pt} \text{OH} & & \text{HO} \rule{1cm}{0.4pt}\!\!\!+\!\!\!\rule{1cm}{0.4pt} \text{H} \\
| & & | \\
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH}
\end{array}
$$

    D – (+) –Glyceraldehyde   L (-) – Glyceraldehyde
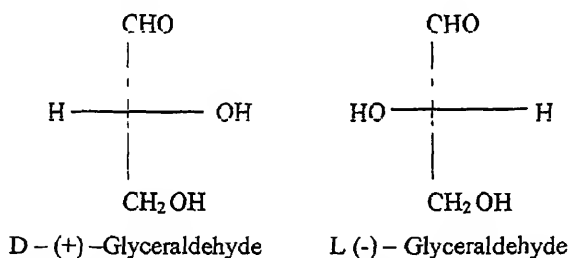
    Taking glyceraldehyde as the reference, all chiral molecules are given the D and L configuration. Now D configuration is assigned to that Chiral molecule in which the carbon atom next to the bottom carbon atom has –OH group attached on R.H.S. in the Fischer's Projection formula keeping the most oxidized Carbon atom at the top of the vertical line. This can be clarified by taking the examples open chain structures of open chain structures of D (+) Glucose and L – (–) – Glucose.

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```
            CHO                           CHO
     H ──────── OH            H ──────── OH
     HO ──────── H            HO ──────── H
     H ──────── OH            H ──────── OH
     H ──────── OH            HO ──────── H
           CH₂OH                     CH₂OH
```

$$\text{D} - (+) - \text{Glucose} \qquad\qquad \text{L} - (-) - \text{Glucose}$$

It may, however, be emphasized in the class that D and L configuration has nothing to do with rotation of the plane polarized beam of light i e. d and l or (+) and (-) D and L do not interfere with d and l or (+) and (-) rotation of the molecule.
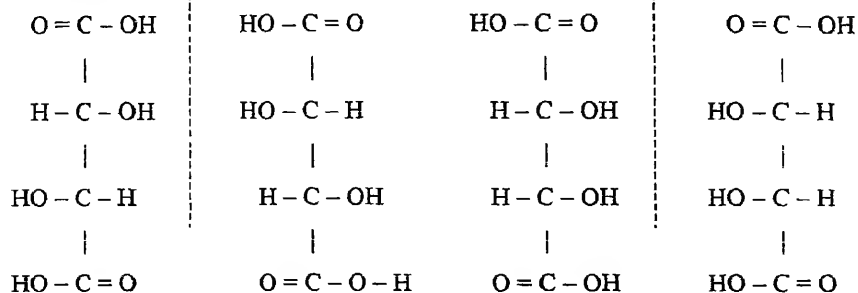
9 Condition for optical Activity

In the beginning it was assumed that presence of asymmetric or chiral carbon atom was the essential condition for any substance to be optically active. Later on it was found that mere presence of Chiral Carbon atom was not enough For example, meso form of tartaric acid inspite of the presence of two Chiral Carbon atoms, happens to be achiral (symmetrical) molecule and can be cut into two identical halves Thus the essential condition for any compound to be optically active is chirality of the molecule on the whole. 2.3-Pentadiene (CH₃ CH = C=CHCH₃) and Trideca 3,5,7,8 – tetraene 10, 12 diynoic acid donot contain any chiral carbon but they show enantiomerism or optical isomerism due to chirality in the molecule. On the contrary, there are compounds, which contain chiral carbon atom, and the molecule is also chiral but the calculated specific rotation of the molecule is too small to be measured by the polarimeter For example , 4-Ethyl – 4 – methyloctane shows rotation of the order of 0.00001° Hence, such a molecule will be considered as optically inactive. Thus it can be inferred that all optically active molecules are chiral but all chiral molecules need not show optical activity

10. Enantiomers and Diastereomers

d-lactic acid and l-lactic acid are mirror images of each ether and they are non-superimposable and show optical activity. They are enantiomers, Similarly the two forms of d-tartaric acid and l-Tartaric acid are the examples of enantiomers, But there is another

form of tartaric acid as mentioned earlier This is meso form. Configurations of various stereoisomers of tartaric acid are given below·

Tartaric Acid

$$
\begin{array}{llll}
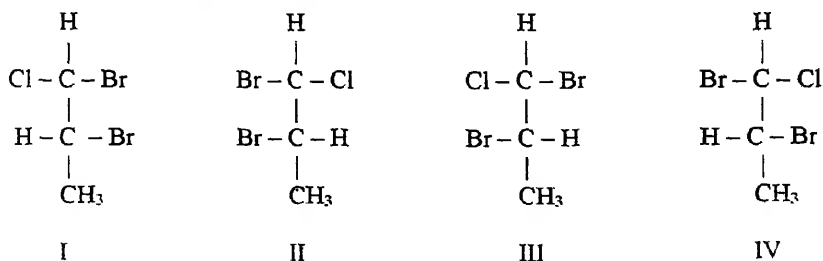O = C - OH & HO - C = O & HO - C = O & O = C - OH \\
| & | & | & | \\
H - C - OH & HO - C - H & H - C - OH & HO - C - H \\
| & | & | & | \\
HO - C - H & H - C - OH & H - C - OH & HO - C - H \\
| & | & | & | \\
HO - C = O & O = C - O - H & O = C - OH & HO - C = O
\end{array}
$$

d – Tartaric acid   l – Tartaric acid   meso-tartaric acid

I   II   III or IIIA

(rotation taking place from H to OH group)   Same

Configuration III and IIIa though mirror images and also contain two chiral carbon atoms but they donot have chilarity in the molecule They have a plane of symmetry and can be cut into two identical halves III and III a are same and donot show optical activity. Form I and III contain Chiral Carbon atoms. They do differ in their configuraton but they are not mirror images and non-superimposable. **Such pairs of stereoisomers which are not mirror images are known as diastereoisomers or diastereomers.**

Let's illustrate by taking another example of 1.2 Dibramo – 1 – Chloro propane which can have the following four stereoisomers.

$$
\begin{array}{llll}
H & H & H & H \\
| & | & | & | \\
Cl - C - Br & Br - C - Cl & Cl - C - Br & Br - C - Cl \\
| & | & | & | \\
H - C - Br & Br - C - H & Br - C - H & H - C - Br \\
| & | & | & | \\
CH_3 & CH_3 & CH_3 & CH_3
\end{array}
$$

I   II   III   IV

The molecule has two chiral carbon atoms Hence it will have 2^n i.e. 2^2 i.e. 4 stereoisomers. (Teachers may emphasise that it is not always necessary that the total number of isomers will be 2^n where n is the number of chiral carbon atoms (Teachers may recall the example of tartaric acid where there are only three stereoisomers. Stereoisomer I and II are mirror image of each other and non-superimposable. Hence I and II are enantiomers Similarly III and IV are also enantiomers But what about I and III , I and IV and , II and III and II and IV? I and III are stereoisomers but they are not mirror images Similarly I and IV are not mirror images. II & III and II & IV are also not mirror images These are diasteromers **Thus it may be remembered that the stereoisomers which are not mirror images are known as diastereoisomers.** This concept may further be strengthened by solving the following exercises:

1. **Draw Configuration of various stereoisomers corresponding to the molecule**
   i. **3 – Chloro butan–2–ol**
   ii. 1 – Iodo – propane - 1,2 – diol
2. Classify the above stereoisomers into enantiomers and diastereomers.

Diastereomers differ from enantiomers in the following aspects :

1. **Enantiomers have same m.p., b.p., solubilities, densities etc. but diastereomers donot.**

2. **Enantiomers are optically active but diastereomers may not be optically active. For example, d – Tartaric acid and meso – Tartaric acid are diastereomers but the former is optically active whereas the later one is not . But stereoisomers I and III i.e. diastereomers of 1,2 – Dibromo – 1 – Chloro propane are optically active.**

3. **Enantiomers cannot be separated by techniques such as fractional crystallization. fractional distillation and chromatography etc. but diastereomers can be separated.**

11. Resolution

It may also be emphasized that during synthesis, we get a mixture of (+) and (-) enantiomers in equal amounts i e. we get a d– l mixture or racemic mixture but any one
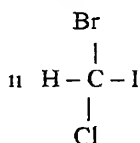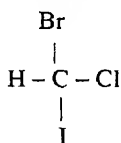
optically active isomer can be separated by adopting special means like hand picking of crystals which are of different shapes or by chemical means i e. by treating with optically active reagent when one of the two enantiomers will react preferably leaving behind the other. Separation of d or l form from dl or recemic mixture is known as resolution After going through this paper, it may be useful to attempt the following exercies.

Exercise

1. Out of staggered and eclipsed conformations of ethane which is more stable and why?

2. According to Baeyer's strain theory, cycloalkanes beyond cyclopentane are found to be almost equally stable. How do you account for this behaviour?

3. Account for the more stability of chair form than the boat form by drawing energy level diagram

4. Both allocinnamic acid and cinnamic acid possess the same molar mass but cinnamic acid has higher m p. than allocinnamic acid. Why?

5. Why does cis – 1,2 - dichloro ethene boils at a higher temperature than trans 1, 2 dichloroethene ?

6. Explain CIP rules for assigning priority to different groups

7. Assign Z and E Configuration to the Geometrical isomers of the following molecules

    i $CH_3CH = CH - CH_3$

    ii $CBrCl = CHI$
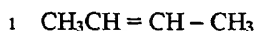
8. Assign R and S configuration to the following molecules:

$$\begin{array}{cc} \text{Br} & \text{Br} \\ | & | \\ \text{H} - \text{C} - \text{Cl} & \text{ii }\ \text{H} - \text{C} - \text{I} \\ | & | \\ \text{I} & \text{Cl} \end{array}$$

9. How do you justify the statement that it is chirality of the molecule and not the mere presence of chiral carbon atom which is responsible for a compound to be optically active?

10. What is the difference between enantiomers and diastereomers? Illustrate your answer by taking examples

ELECTRONIC APPROACH OF TEACHING OF HYDROCARBONS

Dr. V.P. Gupta

1. INTRODUCTION

Unit of hydrocarbons consists of alkanes, cycloalkanes, alkenes, alkynes, alkadienes and arenes like benzene and toluene. After discussing classification nomenclature and isomerism in various kinds of hydrocarbons (chain, conformations and enantiomerism in alkanes; chain, position and geometrical in alkenes; chain and position in alkynes and arenes), major part of this unit can be covered by following the electronic approach of teaching with the help of which why and how of many reactions of hydrocarbons can be better understood in a logical manner involving basics of reaction mechanism which will give ample opportunities to students for brain storming and help in inculcating scientific attitude. An effort has been made in this paper to learn different aspects of this unit through reaction mechanism.

2. Substitution Reactions of Alkanes

Alkanes show substitution reactions like halogenation, nitration and sulphonation. These reactions are found to follow free radical mechanism. Cracking of alkanes, ozonolysis of alkenes and alkynes and hydrogenation reactions of alkenes and alkynes are found to involve free radicals. As an example, free radical mechanism of chlorination of methane may be discussed in Class XI in detail as given below:

2.1 Free Radical Chain Mechanism of Chlorination of Methane

Mixture of methane and chlorine gas on being kept in a flask in diffused sunlight forms chloromethane. Dichloromethane, trichoromethane and tetrachloromethane have also been reported alongwith chloromethane if chlorine gas is taken in excess. In this case let's restrict ourselves to the formation of chloromethane for which the reaction can be written as:
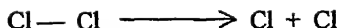
$$CH_4 \text{ (g)} + Cl_2 \text{ (g)} \xrightarrow{E\,=\,h\nu} CH_3Cl + HCl$$
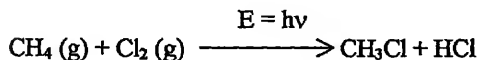
This reaction is supposed to proceed in the following steps:

a. Initiation

Chlorine molecule undergoes homolysis in the presence of diffused sunlight to form chlorine free radicals:

$$E = h\nu$$

$$Cl-Cl \longrightarrow Cl + Cl$$
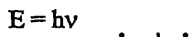
b. **Propagation**

i) Chlorine radical being highly unstable and reactive attacks the methane molecule to facilitate homolysis of $C-H$ bond thus giving rise to $\overset{.}{C}H_3$ and HCl

Methyl free radical
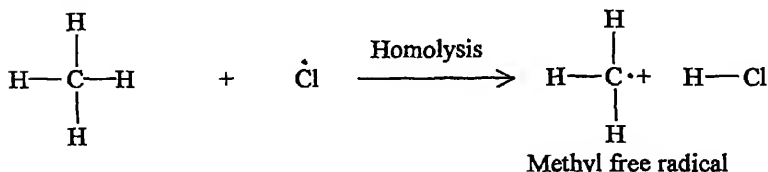
ii) Methyl free radical thus obtained attacks another chlorine molecule, which undergoes homolysis to form $CH_3 - Cl$ alongwith the production of another chlorine free radical.
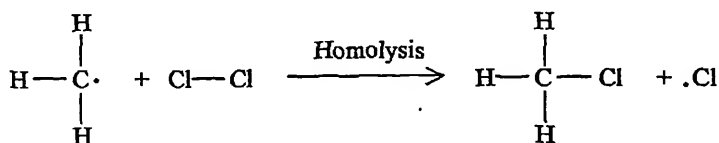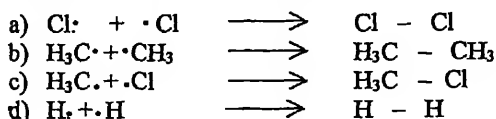

Thus the formation of both the products CH_3 Cl and HCl is accounted for. It may be remembered here that consumption of one free radical gives rise to another free radical and this process continues. That is why such a type of reaction is supposed to proceed via free radical chain substitution mechanism.

c. **Termination**

The reaction cannot proceed indefinitely. It is observed that the reaction comes to a standstill after some time. It may be due to two factors.

i) When the number of effective collisions between a free radical and the reactant molecule is reduced appreciably due to decrease in concentration of the reactants and

ii) When one free radical bombards or combines with another free radical to form a molecule. This leads to termination of the reaction. This step is known as termination and may be due to the following side reactions.
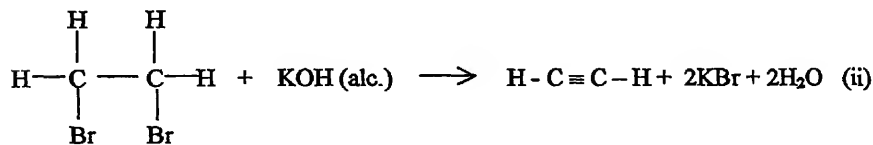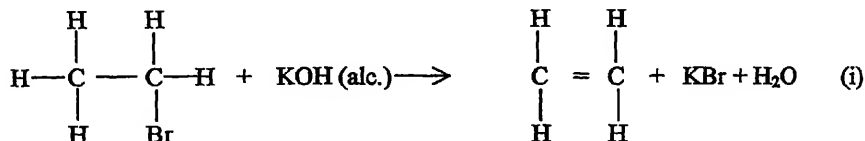
a) $Cl\cdot\ +\ \cdot Cl \longrightarrow Cl\ -\ Cl$
b) $H_3C\cdot + \cdot CH_3 \longrightarrow H_3C\ -\ CH_3$
c) $H_3C\cdot + \cdot Cl \longrightarrow H_3C\ -\ Cl$
d) $H\cdot + \cdot H \longrightarrow H\ -\ H$

From the above reactions, it is clear that H_2 and C_2H_6 gases are obtained as by-products. This is how the formation of small amount of C_2H_6 and H_2 gases can be explained during chlorination of methane. Though reaction (iii) accounts for the formation of CH_3Cl one of the products but in this step combination of two free radicals leads to

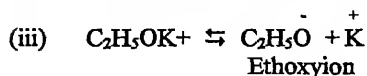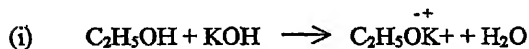decrease in concentration of the free radicals and hence responsible for termination of the reaction.

3. Preparation of Alkenes and Alkynes by Dehydrohalogenation

Monohologen derivatives and vicinal dihologen derivatives of alkanes of treatment with alkcoholic KOH undergo elimination of Hx to form alkenes and alkynes respectively. The reation can, in simple terms be represented as:
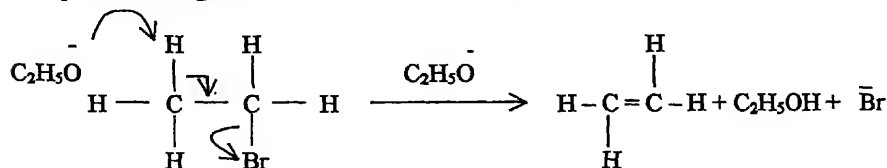
$$
\begin{array}{c}
\text{H} \quad \text{H} \\
\text{|} \quad\quad \text{|} \\
\text{H}-\text{C}-\text{C}-\text{H} + \text{KOH (alc.)} \longrightarrow \\
\text{|} \quad\quad \text{|} \\
\text{H} \quad \text{Br}
\end{array}
\qquad
\begin{array}{c}
\text{H} \quad \text{H} \\
\text{|} \quad\quad \text{|} \\
\text{C} = \text{C} + \text{KBr} + \text{H}_2\text{O} \qquad \text{(i)} \\
\text{|} \quad\quad \text{|} \\
\text{H} \quad \text{H}
\end{array}
$$

$$
\begin{array}{c}
\text{H} \quad \text{H} \\
\text{|} \quad\quad \text{|} \\
\text{H}-\text{C}-\text{C}-\text{H} + \text{KOH (alc.)} \longrightarrow \text{H}-\text{C} \equiv \text{C}-\text{H} + 2\text{KBr} + 2\text{H}_2\text{O} \quad \text{(ii)} \\
\text{|} \quad\quad \text{|} \\
\text{Br} \quad \text{Br}
\end{array}
$$

These reactions in which Br (or x) from one carbon and one hydrogen atom from the Beta (β) carbon atom are lost as Hx are known as Dehydrohalogenation reactions. These are also known as β-elimination reactions because hydrogen atom from β-carbon atom is removed. Let's understand mechanism of reaction (i).

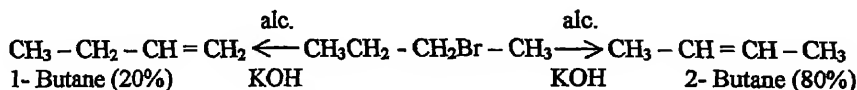**Mechanism:** Alcoholic KOH means KOH dissolved in alcohol, which will give rise to potassium ethoxide.

(i) $C_2H_5OH + KOH \longrightarrow C_2H_5\overset{\cdot+}{O}K + + H_2O$

(ii) $C_2H_5\overset{\cdot+}{O}K$ being an ionic molecule ionizes to give $C_2H_5\overset{\cdot}{O}$ and $\overset{+}{K}$

(iii) $C_2H_5OK+ \leftrightarrows C_2H_5\overset{\cdot}{O} + \overset{+}{K}$
               Ethoxyion

Ethoxy ion being a strong base tends to abstract any one of H atom, which is β to the Br atom as H^+, which is further, facilitated due to the more electronegative nature of Br atom than the carbon atom. The cleavage of C – H and C - Br bonds require energy and this comes from (a) the formation of the bond between the abstracted H^+ and ethoxy ion and (b) formation of the H bond and (c) the energy of salvation of the halide ion. This can be represented as given below: -

$$
\begin{array}{c}
\overset{-}{C_2H_5O} \\
\\
\text{H}-\overset{\text{H}}{\underset{\text{H}}{\overset{|}{C}}} \overset{\text{H}}{\underset{\text{Br}}{\overset{|}{C}}} - \text{H}
\end{array}
\longrightarrow
\begin{array}{c}
\overset{-}{C_2H_5O} \\
\\
\text{H}-\overset{\text{H}}{\overset{|}{C}} = \overset{\text{H}}{\underset{\text{H}}{\overset{|}{C}}} - \text{H} + C_2H_5OH + \overset{-}{Br}
\end{array}
$$

Dehydrohalogenation generally proceeds in such a way that the more stable (the more highly substituted alkene) is the major product. For example, 2-Bromo butane on Dehydrohalogenation forms 2-butene as the major product:

$$CH_3 - CH_2 - CH = CH_2 \xleftarrow[KOH]{alc.} CH_3CH_2 - CH_2Br - CH_3 \xrightarrow[KOH]{alc.} CH_3 - CH = CH - CH_3$$

1- Butane (20%)   2- Butane (80%)

Relative Reactivities of Alkylhalides

The decreasing order of reactivity of alkyl halides is found in the order:

tert—Alkylhalides>Sec-Alkylhalides> Primary alkyl halides. It is clear that the branching around carbon carrying the halogen increase as we have along the series from primary to tertiary alkyl halides. The greater the branching, the greater is the number of hydrogens which would be available for attack by the base, hence, the more favourable probability factor for elimination. Moreover, the more branched alkylhalide leads to the formation of a more highly branched and more stable alkene.

4.   **Preparation of Alkenes by Acidic Dehydration of Alcohols**

Alcohols on heating with concentrated sulphuric acid undergo dehydration to form alkenes. For example, on heating with conc. H_2SO_4 at 443K forms ethene with the loss of one water molecule as shown below.
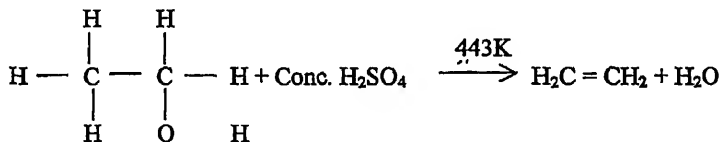
Mechanism

This reaction is supposed to proceed via the formation of a carbonium ion from the protonted alcohol.

(i) $H_2SO_4 \leftrightarrows H^+ + HSO_4$

Protonted alcohol

44

$$H \quad \overset{\oplus}{O} - H \qquad\qquad H$$
$$\underset{H}{|}$$
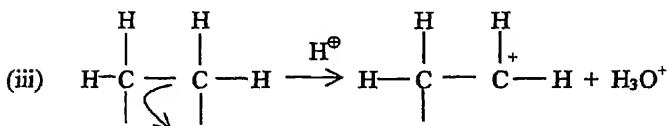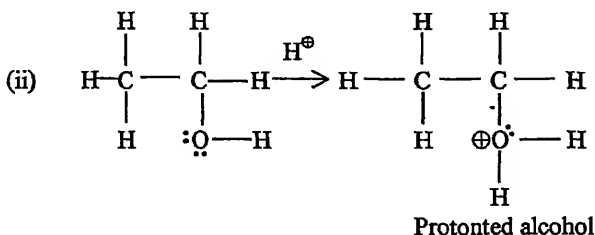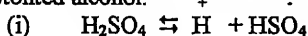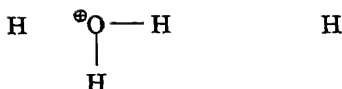
(iv) HSO_4^- attacks the carbonium ion (Carbocation) and at higher temperature (443k) abstracts one H atom in the form of a proton from the carbon β to the carbonium ion to form ethene.

$$HSO_4^- \quad \overset{H}{\underset{H}{\overset{|}{C}}} \quad \overset{H}{\underset{\oplus}{\overset{|}{C}}} \quad H \xrightarrow{\ HSO_4\ } H - \overset{H}{\underset{H}{\overset{|}{C}}} = C - H + HSO_4$$
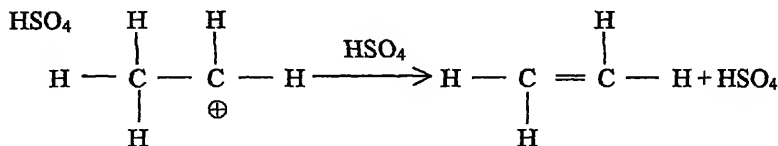
Since carbonium ion is the intermediate, tertiary alcohols ore found to undergo acidic dehydration more easily due to the formation of the most stable tertiary carbonium ion. Thus the pattern of acidic dehydration of alcohols is found to be:

Tertiary > secondary > primary

Think over
Why 2-Butene is the major product during acidic dehydration of 1-Butanol?

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5.   Electrophilic Addition Reactions

Carbon-Carbon double and triple bonds, which are electron rich, react with electrophiles (electron seeking reagents) to give addition products. These reactions proceed by a polar mechanism involving carbonium ion and sometimes the cyclic halonium ion as the intermediate. Electron donating substituents on the olefin accelerate the rate of the reaction. The addition of any reagent $X - Y$ to cyclic and acyclic olefins usually occurs with trans stereochemistry as given below:

$$\underset{H}{\overset{H}{\diagdown}} C = C \overset{H}{\underset{H}{\diagup}} \quad + \quad X - Y \longrightarrow \underset{H}{\overset{H\quad X}{\diagdown|}} C - \underset{Y\quad H}{\overset{}{|\diagup}} C$$
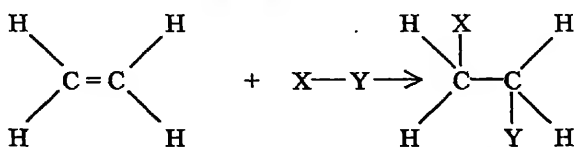
5.1   Electrophilic Addition Reaction of Bromine and Alkenes

Bromine molecule undergoes heterolysis to form Br^+ and Br^-. Br^+ being the electrophile attacks the alkene molecule in which electromeric effect (migration of electron from less electro-negative to more electro-negative atom) takes place to form the intermediate carbonium ion (cyclic halonium ion formation has also been reported by Robertson but not discussed at this level). The atom from which electron migration takes place becomes positively charged and at which migration takes placed becomes negatively charged. Br^- later on combines with the carbonium ion to form the 1, 2 dibromo addition product. Mechanism of addition reactions of bromine with ethene and propene are given below:
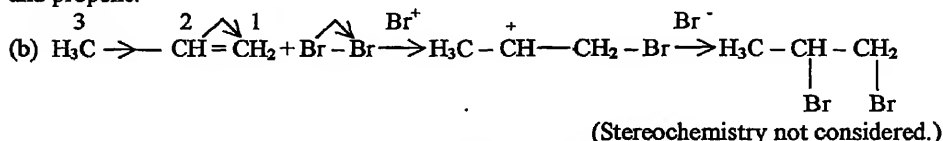
a) $CH_2 = CH_2 + Br — Br \longrightarrow$ $\begin{array}{cc} H_2C — CH_2 \\ | \quad\quad | \\ Br \quad\quad Br \end{array}$

(Stereo Chemistry not considered)
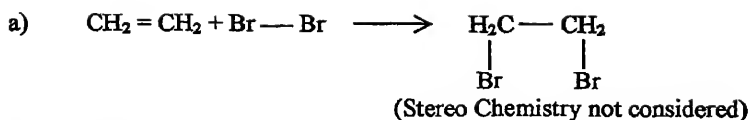
Mechanism

Stepwise mechanism is given for simplicity sake but it never means that one step is being followed by the other;

Heterolysis

i) $Br – Br \xrightarrow{\quad\quad\quad} Br^+ + Br^-$

ii) $H_2\overset{\frown}{C} = CH_2 \xrightarrow{Br^\oplus} H_2\overset{+}{C} — \underset{\underset{Br}{|}}{CH_2} \xrightarrow{Br^-} \underset{\underset{Br}{|}}{H_2C} — \underset{\underset{Br}{|}}{CH_2}$

(Stereochemistry not considered)
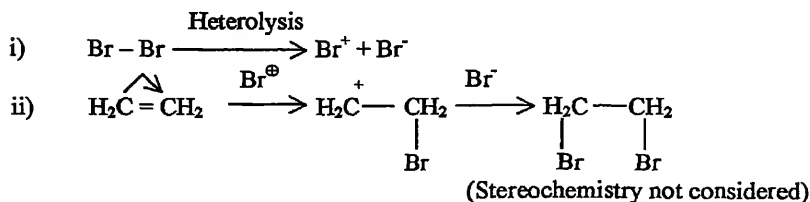
After understanding the above mechanism, we can write the addition reaction of Br_2 and propene.

(b) $\overset{3}{H_3C} \overset{\frown}{\longrightarrow} \overset{2}{\overset{\frown}{CH}} = \overset{1}{CH_2} + \overset{\frown}{Br} – Br \xrightarrow{Br^+} H_3C – \overset{+}{CH} — CH_2 – Br \xrightarrow{Br^-} H_3C – \underset{\underset{Br}{|}}{CH} – \underset{\underset{Br}{|}}{CH_2}$

(Stereochemistry not considered.)

In this case it may be remembered that in propene, electrometric effect will take place from carbon 2 to carbon 1 and not vice versa due to the electron donating nature of methyl group.

5.2   Electrophilic Addition Reactions of Bromine and Alkynes

Alkynes like ethyne and propyne also undergo electrophilic addition reactions with halogens to form tetrahalogen compounds. For Example,

$HC \equiv CH + 2Br_2 \longrightarrow CHBr_2 – CHBr_2$

Mechanism

In this case two molecules of Bromine add to one molecule of ethyne to from 1, 1, 2, 2 tetrabromethane. It may be remembered that Carbon atom from which electron is shifted gets positively charged and the other one at which electron is shifted becomes negatively charged. The negatively charged carbon ion combines with the positively charged Br^+ to form a new bond between carbon and bromine. Similarly the positively charged carbon ion and the Br $^-$ combines to form another bond between carbon and bromine to form the addition product as shown below:

$H—\overset{\frown}{C} \equiv C — H + Br\overset{\frown}{—}Br \xrightarrow{Br^+} H — \underset{\underset{Br}{|}}{\overset{+}{C}} = C—H \xrightarrow{Br^-} H — \underset{\underset{Br}{|}}{C} = \underset{\underset{Br}{|}}{\overset{\frown}{C}} — H$

$\underset{\underset{|}{H}}{H — \underset{\underset{|}{Br}}{C} — \underset{\underset{Br}{|}}{C} — H} \overset{Br^-}{\underset{\quad}{\longleftarrow}} H — C^+ — \underset{\underset{Br}{|}}{C} — H \overset{Br^+}{\underset{Br—Br}{\longleftarrow}}$

46
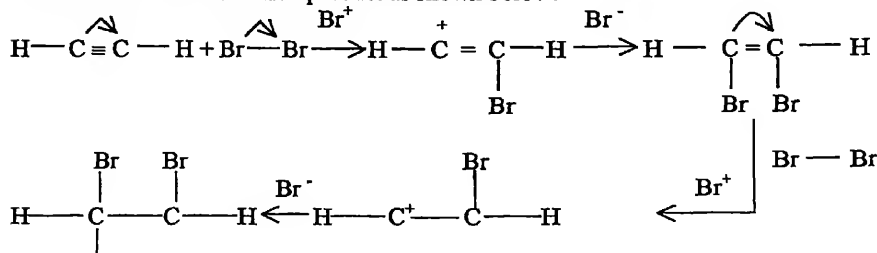
Br	Br		Br	Br

1, 1, 2, 2- tetrabromothane

Let's now write the addition product of reaction between propyne and two molecules of Br_2.

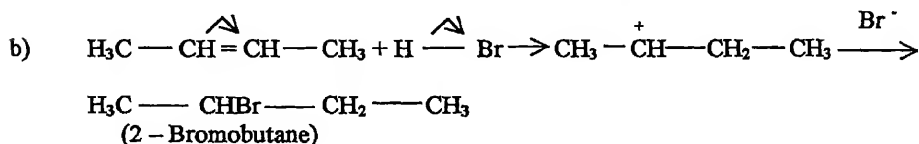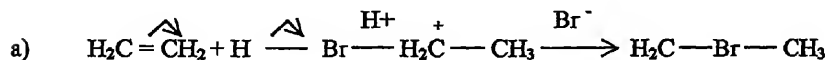i) $H_3C - C \equiv C - H + Br \overset{\wedge}{\underset{\wedge}{\longrightarrow}} Br \xrightarrow{Br^+} H_3C - \overset{+}{C} = C - H$

$H_3C - C = C - H$ with Br and Br^-

$$\underset{Br}{\underset{|}{\overset{3}{H_3C}}} - \underset{|}{\overset{2}{C}} = \underset{|}{\overset{1}{C}} - H$$

Br   Br
(1, 2 –dibromopropene)

$$H_3C - \overset{\oplus}{\underset{Br}{\overset{|}{C}}} - \overset{|}{\underset{Br}{C}} - H \xrightarrow{Br^-}$$

(ii) $H_3C - \hat{C} = \hat{C} - H + Br - Br \xrightarrow{Br^+} H_3C - \overset{\oplus}{\underset{Br}{\overset{|}{C}}} - \underset{Br}{\overset{|}{C}} - H \xrightarrow{Br^-}$

Br Br

$$H_3C - \underset{Br}{\overset{\overset{Br}{|}}{C}} - \underset{Br}{\overset{\overset{Br}{|}}{C}} - H$$
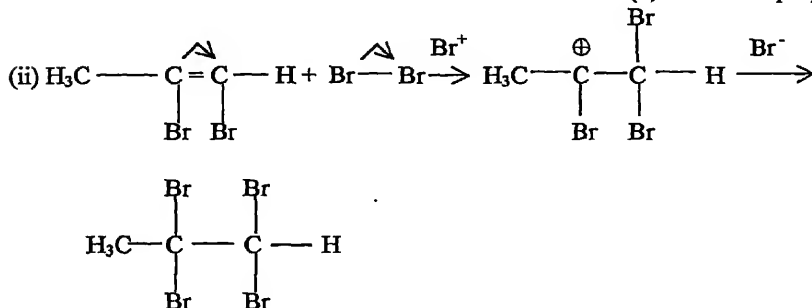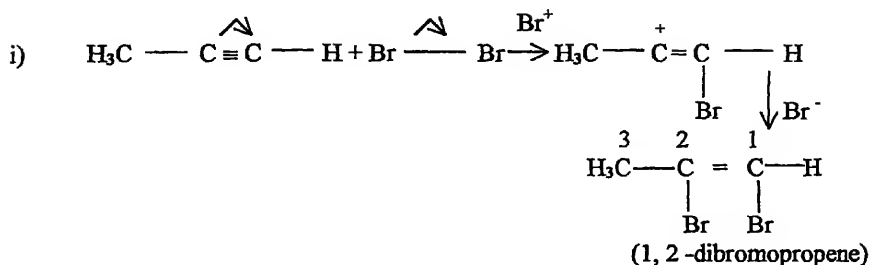
(1, 1, 2, 2 -tetrabromopropane)

> **Think over:**
> Out of ethene and ethyne, which will undergo Electrophilic addition reactions easily & why?

5.3 Electrophilic Addition Reaction of HBr to Symmetrical Alkenes

Addition reactions of HBr to symmetrical alkenes take place as per Electrophilic addition mechanism as mentioned earlier and the product formation is easily predicted. In case of ethene, bromoethane is the product and in case of 2-Butene, 2 - Bromobutane will. be the product.

a) $H_2C = CH_2 + H \overset{\wedge}{\underset{\wedge}{\longrightarrow}} Br \xrightarrow{H+} \overset{+}{H_2C} - CH_3 \xrightarrow{Br^-} H_2C - Br - CH_3$

b) $H_3C - CH = CH - CH_3 + H \overset{\wedge}{\longrightarrow} Br \xrightarrow{} CH_3 - \overset{+}{CH} - CH_2 - CH_3 \xrightarrow{Br^-}$

$H_3C - CHBr - CH_2 - CH_3$
(2 – Bromobutane)

5.4 Electrophilic Addition Reaction of HBr to unsymmetrical Alkenes (Markovnikov Rule)

$$CH_3 - CH = CH_2 + H - Br \longrightarrow
\begin{bmatrix}
CH_3 - CH - CH_3 \\
\quad\quad\quad | \\
I \quad\quad Br \quad \text{(Major Product)} \\
\\
CH_3 - CH_2 - CH_2 - Br
\end{bmatrix}$$

II   (Minor Product)
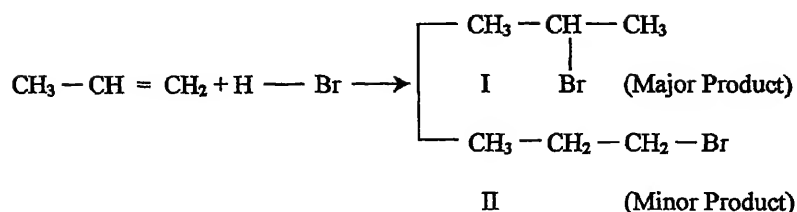
Markovnikov, a Russian Chemist who made a generalization in 1869 in the form of a rule called Markovnikov rule, studied such reactions in detail. The rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms. Thus according to this rule product I i.e. 2 – Bromopropane is expected and this is found as the actual major product in this reaction.

The above generalization of Markovnikov Rule can be better understood in terms of mechanism.

Mechanism

As soon as H – Br comes in contact with propene, HBr molecule provides H^+. The electrophile H^+ obtained from H – Br attacks the propene molecule in which the double bond undergoes electromeric effect from C_2 to C_1 due to the electron donating effect (+1) of the methyl group to form the Carbonium ion.

(i)
$$\overset{3}{H_3C} - \overset{2}{CH} = \overset{1}{CH_2} + H - Br \overset{H+}{\longrightarrow} H_3C - \overset{+}{CH} - CH_3$$
$$\text{Carbonium ion}$$
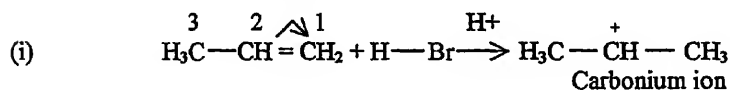
The carbonium ion will be attacked by Br^- to form
$$CH_3 - CH - CH_3$$
$$\quad\quad\quad |$$
$$\quad\quad\quad Br$$

$$H_3C - \overset{+}{CH} - CH_3 \overset{Br-}{\longrightarrow} H_3C - \underset{|}{CH} - CH_3$$
$$\underset{\quad\quad\quad Br}{}$$
$$\text{2 – Bromopropane (Major)}$$
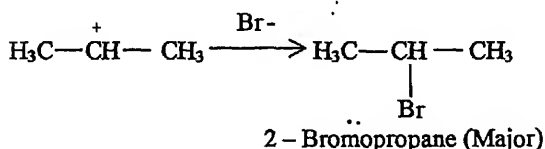
The formation of 2- Bromopropane as the major product and not 1 – Bromopropane can also be better understand in terms of stability of the secondary carbonium ion,

$$\begin{array}{c} CH_3 \\ \overset{+}{} \\ CH_3 \end{array} \!\!\! > CH$$ as compared to the primary carbonium ion $CH_3CH_2\overset{+}{C}H_2$ as already Discussed.

i) $$CH_3 \!\!>\!\! - CH = CH_2 \longrightarrow CH_3 - \overset{+}{CH} - CH_3$$
$$\text{(More stable sec. carbonium ion)}$$

ii) $CH_3 \overset{H^{\oplus}}{\longrightarrow} CH = CH_2 \longrightarrow CH_3 \overset{+}{—CH_2—CH_2}$

(Less stable Pmy Carbonium ion)
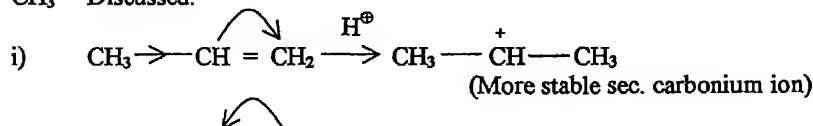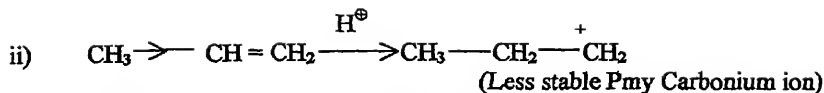
Markovinkov rule has now been extended to the addition of all unsymmetrical reagents (H_2SO_4, CH_3COOH, $HOCl$, $NOCl$, H_2O) to unsymmetrical alkenes. The modern version of the Markovnikov rule is that Electrophilic addition to carbon - carbon double bound involves the intermediate formation of the more stable carbonium ion. The rule can be useful for predicting the addition reaction products with alkynes also.

> **Just Try**
> Write the Electrophilic addition reaction of acetic acid with ethyne and propyne.

5.5   Anti Markovnikov Addition or Peroxide Effect or Kharash Effect

Addition of HBr to unsymmetrical alkenes like propene in the presence of light or peroxide takes place contrary to the Markovnikov rule. This so happens only with HBr but not with HCl and HI. This departure from the rule is known as the peroxide or Kharash effect or anti Markovnikov addition.

$$CH_3—CH = CH_2 + HBr \xrightarrow{(C_6H_5CO)_2\ O_2} CH_3—CH_2—CH_2Br$$
$$1-Bromopropane$$
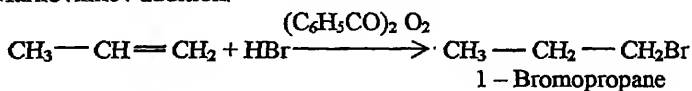
Mechanism: Peroxide effect proceeds via free radical mechanism as given below:

i) $C_6H_5—\overset{O}{\overset{\|}{C}}—O—O—\overset{O}{\overset{\|}{C}}—C_6H_5 \xrightarrow{Homolysis} 2C_6H_5—\overset{O}{\overset{\|}{C}}—\dot{O} \rightarrow 2\dot{C_6H_5} + 2CO_2$

ii) $\dot{C_6H_5} + H—Br \xrightarrow{Homolysis} C_6H_6 + \dot{Br}$

iii) $CH_3——CH = CH_2 + \dot{Br} \xrightarrow{Homolysis} CH_3——\dot{CH}—CH_2—Br.$
$$(Sec.\ free\ radical)$$

iv) $CH_3——\dot{CH}—CH_2Br + H—Br \xrightarrow{Homolysis} CH_3——CH_2—CH_2Br + \dot{Br}.$
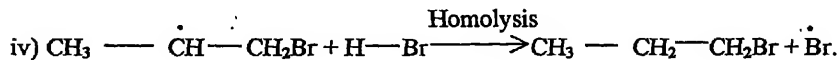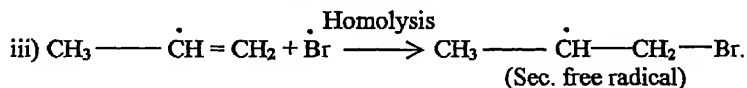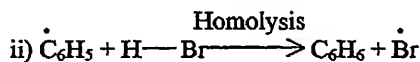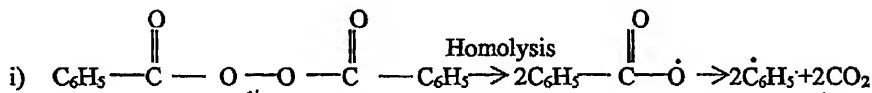
The secondary free radical obtained in (iii) in the above mechanism happens to be more stable than the primary one & hence explains the formation of n – propylbromide.

It may be noted that the peroxide effect is not observed in addition of HCl and Hl. This may be due to the fact that the H – Cl bond being stronger (430.5 kJ mol^{-1}) than H – Br bond (363.7 kJ mol^{-1}), is not cleaved symmetrically by the free radical. The H – 1 bond is weaker (296.8 kJ mol^{-1}) and iodine atoms couple to form iodine molecules rather than to add to the double bond. Hence, peroxide effect is observed only in case of addition of H – Br to unsymmetrical alkenes.

6.   Electrophilic Substitution Reactions

If the electrophile (E^+) is involved in replacement or substitution, the reaction is said to be Electrophilic substitution reaction and abbreviated as S_E. Halogenation, nitration, sulphonation, alkylation and accetylation reactions (Friedel-Craft reaction) of benzene are the examples of S_E reactions. Mechanisms of a few S_E reactions are discussed below:

6.1 Chlorination of Benzene

Benzene on treatment with Cl_2 in cold, dark and in the presence of anhydrous $AlCl_3$ forms Chlorobenzene.
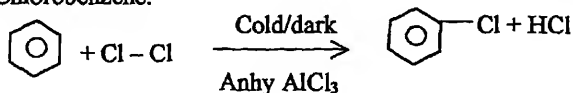
One questions arises in our mind: What is the role of anhy. $AlCl_3$ in this reaction? One answer can be that it acts as a catalyst. Then the next question would be: How does it act as a catalyst? Answer to this problem can be found in mechanism. Let's have a look on the mechanism of this reaction.

Mechanism

i) $AlCl_3$ behaves as a Lewis Acid due to deficiency of electrons. Being a Lewis acid, it helps in the hetrolysis of $Cl - Cl$ bond to generate Cl^+ (Chloronium ion) and to

form $\overset{..}{Cl}$ $AlCl_3$.
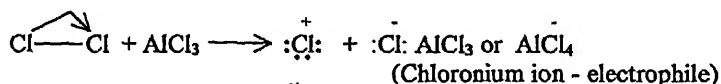
ii)   The Chloronium ion (Cl^+) being an electrophile attacks the benzene molecule, a good source of loosely held π electrons in which one of the double bonds undergoes electrometric effect and carbocation (I) is formed. This can be understood by considering one of the Kekule's structures of benzene.

(I)
(Carbonation)
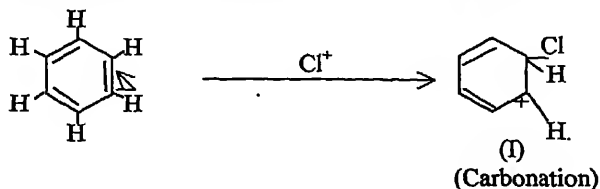
The Carbocation (I) is resonance stabilised, as we know that more the resonance more is the stability. Due to resonance the +ve charge will not be located at any one C atom rather it will be delocalised on many carbons as shown below:
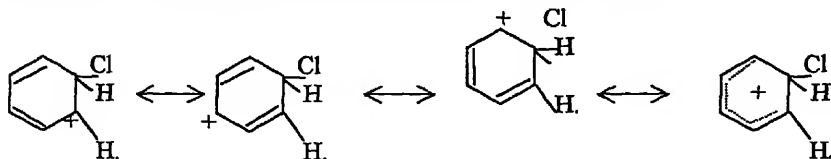
iii)   The carbocation (I) will be attacked by Cl AlCl₃ to abstract H atom attached to the
         C atom to which Cl atom is attached in the form of H+ to form Chlorobenzene and
         HCl and liberating AlCl₃.
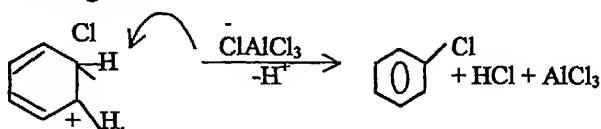
It may be remembered that the role of AlCl₃ during
chlorination of benzene is to generate the chloronium ion, the
electrophile that is the attacking reagent.

6.2   Friedel Craft's Alkylation Reactions

Benzene on treatment with alkyl halides in the presence of anhydrous AlCl₃ forms
alkyl derivatives of benzene. This alkylation reaction is known as Friedel Craft's reaction.
With methyl and ethyl halides, methyl and ethyl derivatives of benzene are obtained but it
may be remembered that with n – propyl chloride, isopropyl benzene and not n–propyl
benzene is the main product.

i)

ii)

iii)
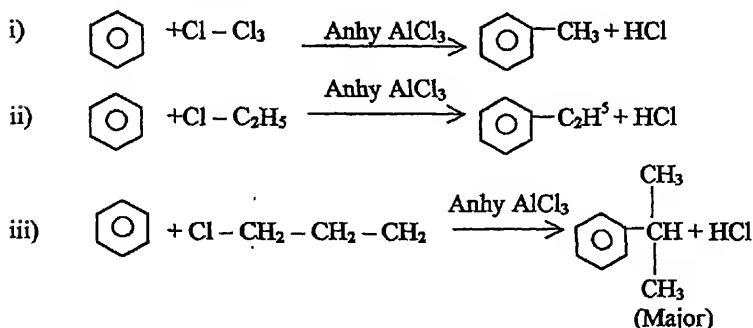
Role of AlCl₃ can be explained only by understanding mechanism of the reaction.
AlCl₃ helps in the hydrolytic fission of C – Cl bond in R – Cl to produce the alkylium ion,
R+ and Cl⁻AlCl₃. As discussed in chlorination of benzene, here R+, the electrophile will
attack the benzene ring in which any one of the three double bonds will undergo
electrometric effect to form the carbocation which will again be resonance stabilized. In
the end, Cl⁻AlCl₃ abstracts H atom attached to the C atom to which the alkyl group is
attached in the form of a proton and alkyl derivative will be obtained. In short, it may be
remembered that during chlorination of benzene, AlCl₃ generates the Chloronium ion
whereas during alkylation, alkylium ion or (R+) is generated.

The formation of isopropyl benzene as the major product on treatment of n – propyl halide with benzene and not n – propyl benzene can also be explained on the basis of the fact that the primary carbonium ion (CH_3-CH_2-$\overset{+}{C}H_2$) generated by $AlCl_3$ tends to convert into the Secondary Carbonium ion ($CH_3 \overset{+}{C}H$ CH_3) as the latter one is more stable than the primary carbonium ion.

$$CH_3 - CH_2 - CH_2 - Cl \xrightarrow{\text{Anhy } AlCl_3} H_3C - CH_2 - \overset{+}{C}H_2 + \overset{-}{Cl}AlCl_3$$

$$CH_3 - CH_2 - \overset{+}{C}H_2 \xrightarrow{\text{Rearranges}} CH_3 - \overset{+}{C}H - CH_3$$
(Primary Carbonium ion)   (Secondary Carbonium ion)
Less Stable   More Stable
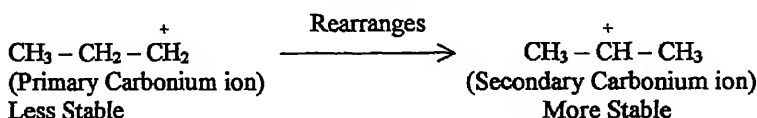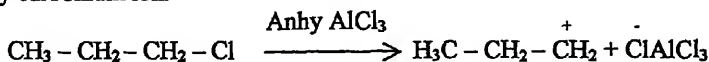
6.3   Friedel Craft's Acetylation Reaction

Reaction of benzene with acetyl chloride in the presence of anhydrous $AlCl_3$ to form acetophenone is the example of Friedel Craft's accetylation reaction.
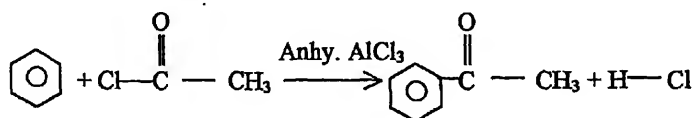
Role of $AlCl_3$ in the reaction is to generate the acetylium ion by hetrolysis of $C - Cl$ bond.
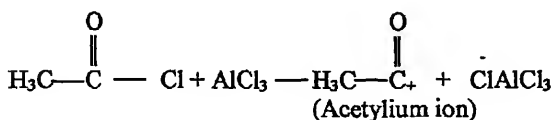
(Acetylium ion)

Acetylium ion, the electrophile is the attacking reagent in this reaction. Rest of the mechanism of this reaction is the same as already discussed in chlorination and alkylation of benzene.

6.4   Nitration of Benzene

Nitration of benzene is another exampled of S_E reaction. Benzene on heating with a mixture of Conc. HNO_3 and Conc. H_2SO_4 forms nitrobenzene.
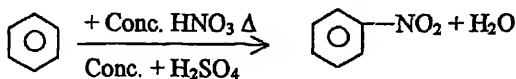
Having a look on this reaction, one fails to understand why H_2SO_4 is taken in this reaction. Role of H_2SO_4 during nitration is again understood by mechanism as given below:

Mechanism:

i) H_2SO_4 being a strong acid ionizes to give a proton and HSO_4. H^+ liberated from H_2SO_4 helps in the generation of Nitronium ion (NO_2) from HNO_3.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

$$H-O-NO_2 \xrightarrow{\text{H+}} H-\overset{\cdot\cdot}{\underset{\underset{Or}{H}}{\overset{+}{O}}}-NO_2 \xrightarrow{\text{H+}} + H_3O^+ + {}^+NO_2$$

(Nitronium ion)

$$2H_2SO_4 + HNO_3 \longrightarrow \overset{+}{NO_2} + H_3O^+ + 2HSO_4^-$$
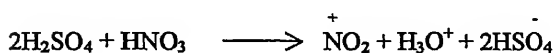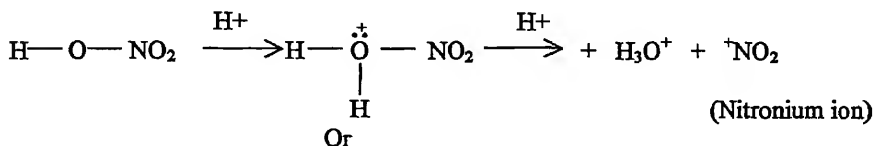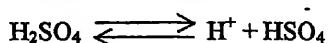
ii) Nitronium ion liberated from HNO_3, being an electrophile attacks the benzene molecule which a good source of loosely held π electrons and one of the double bonds of benzene ring in Kelule structure (Position of double bonds in benzene is not fixed) undergoes electrometric effect to produce the carbonium ion (carbocation)

N^+O_2
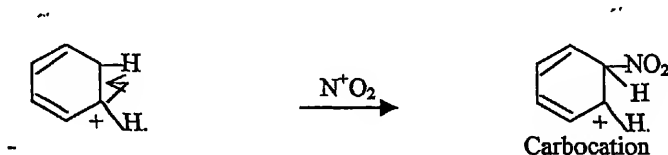
Carbocation

iii) HSO_4 attacks the carbocation and abstracts H atom attacked to the carbon atom to which $- NO_2$ gp is attached in the form of H^+ thus forming nitrobenzene.

HSO_4

$-NO_2 + H_2SO_4$
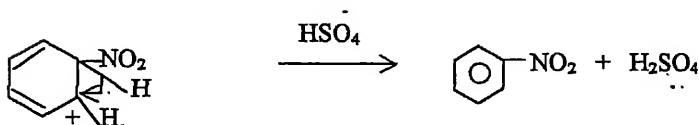
| Write mechanism of sulphonation of benzene |

7. Conclusion

Understanding of mechanisms of the above mentioned free radical substitution, Electrophilic addition, Electrophilic substitution and elimination reactions and practice of other such reactions may give answers of many problems arising in the minds of students when they are learning different methods of preparation and properties of compounds. It may be noted that it is the beauty of organic chemistry that here properties of one class of compounds constitute methods of preparation of the other class. For example, while studying the methods of preparation of alkanes, alkenes, alkynes and benzene, a few properties of the halogen derivatives, alcohols etc. are bound to occur. Hence, it is hoped that teachers will lay emphasis on the fundamentals of organic chemistry, discuss principles in detail and appreciate the role of electron in understanding chemistry of carbon compounds. Why and how of most of the reactions can be understood in terms of electronic approach of teaching. Teachers are requested to attempt the exercise after going through this paper.

Exercise

1. Which of the following is the attacking reagent during reaction of n-propyl chloride with benzene.

(A) $CH_3CH_2\overset{+}{C}H_2$ (B) $CH_3\overset{+}{C}HCH_3$

(C) $CH_3\ \overset{.}{C}H_2\ CH_2$ (D) $CH_3\overset{.}{C}HCH_3$

2. What is the role of conc. H_2SO_4 during nitration of benzene?
3. How do you account for the formation of C_2H_6 during chlorination of methane?
4. what is the major product of formation during addition reaction of H-Br with

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2$$
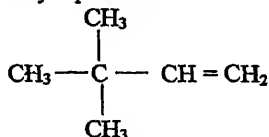
5. Out of 2-Methyl-2-propanol, 2-Methyl-1-propanol, 1-Butonol and 2-Butanol which undergoes acidic dehydration most easily and why?
6. Out of $(CH_3)_3$ C-Br and CH_3 Br which will give pale yellow precipitate with aqueous $AgNO_3$ and Why?
7. Which of the following is the attacking reagent during sulphonation of benzene?

(a) $\overset{.}{H}SO_4$ (b) SO_3 (c) $\overset{..}{S}O_3$ (d) $\overset{..}{S}O_4$

8. Arrange the following halogens in decreasing order of their reactivity with alkanes and also give reasons.
I_2, Cl_2, Br_2.
9. Classify the following into electrophiles & nucleophiles.
$CH_3COCl, BF_3, C_2H_5NH_2, NO_2$
10. Which product will be obtained by the addition of HCl to $CF_3-CH=CH_2$ in presence of peroxide & why?
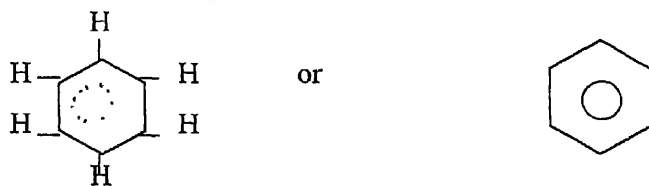
AROMATICITY

Dr. V.P. Gupta

INTRODUCTION

Benzene molecule, the backbone of modern world has been of great interest to chemists for the last about 175 years when it was discovered in 1825. There has been a lot of discussion about the structure of benzene since then, starting from open chain structures to the ring structure proposed by August kekule when he conceived the idea of closed chain (Morrison 2001) of carbon atoms based upon the famous dream which he had in 1858. Later on, developments of resonance, molecular orbital theory and X ray diffraction could establish that all the six carbon - carbon bond lengths in benzene are identical (139pm) and the pi(π) electron cloud of the two neighbouring carbon atoms can lie in either direction but perpendicular to the plane of C-C sigma (σ) bonds. Thus, benzene since 1931 has been represented by a regular hexagon with a circle inside describing delocalisation of the six π electron cloud between the six carbon atoms present at each corner of the regular hexagon as shown below :

Benzene

2   Old Concept of Aromaticity:Benzene and its derivatives like toluene, xylene, phenol, aniline, benzaldehyde etc. possessed unique aroma

(fragrance). Such compounds having a benzene ring associated with unique fragrance (Jan 2001) and possessing the following properties were termed 'Aromatic' compounds.

(i)   m.f. C_6H_6 suggests high degree of unsaturation in the molecule but does not respond positively to the unsaturation tests like bromine test, Baeyer's test and does not show addition reactions at room temperature. On the contrary, benzene shows electrophilic substitution reactions like alkylation, acetylation, hologenation, nitration, sulphonation, which are not shown by open chain unsaturated compounds.

(ii)   Benzene has a ring with alternate double and single bonds position of which is not fixed.

(iii)   Because molecule is found to possess a planar geometry.

(iv)   Benzene is found to be a highly stable molecule as suggested by heat of hydrogenation and heat of combustion data if compared to a cyclic compound with three double bonds i.e. cyclohexatriene (Heat of hydrogenation of benzene : 212 kJmol^{-1}, Heat of hydrogenation of cyclohexatriene: 363kJmol^{-1}, heat of combustion of benzene : 3301.6and   heat of combustion of cyclohexatriene: 3446.8kJ mol^{-1}).

Compounds possessing benzene ring and showing the above properties were called benenoid aromatic compounds. The characteristic of unique stability of such benzene compounds associated with the above unique properties was termed as aromaticity. It was thought that a sextet of π electrons was essential for showing aromaticity.

3. Hückel Theory of Aromaticity

A large number of compounds other than benzene and derivatives also exhibited stability and properties similar to benzene and its derivatives.

Hence, presence of benzene ring was not considered as an essential condition for aromaticity. Erich Huckel of the institut für theoretische Physik Stuttgart gave theory of aromaticity in 1938, popularly known as Hückel theory. Aromaticity is related to electronic structure of the compound. Any compound or ion heterocyclic, monocarbocyclic, or polynuclear may be aromatic if it possesses a specific electronic structure. Hückel theory is based on quantum mechanics, and has to do with the filling up of the various orbitals which make up the π cloud in the cyclic system ; Hückel stated that any planar, cyclic, conjugated system containing $(4n+2)$ π electrons where n is an integer experiences unusual aromatic stabilization, whereas those containing $4n$ π electrons do not (Fox, 1994). This rule is known as Hückel's rule of aromaticity. Main postulates of the Hückle theory are ·

1. An aromatic compound must contain cyclic clouds of delocalised π electrons above and below the plane of the molecule.

2. An aromatic compound must be a flat or a nearly flat molecule to ensure complete or maximum overlap of p-orbitals.

3. π cloud of the cyclic system (molecule or ion) must contain a total of $4n+2$ electrons, where n is an integer (0,1,2 ...). This requirement of π electrons for a molecule/ion to be aromatic is known as the Hückel $(4n+2)$ π electron rule.

4. Cyclic compounds with $4n$ π electrons would be less stable than their open chain counterparts. Such cyclic compounds with $4n$ π electrons are called anti-aromatic compounds.

Illustrations

Following examples can be considered for illustrating the Hcke! rule of aromaticity:

A. Benzenoid compounds

(i) Benzene

Each carbon atom in benzene is sp^2 hybridised. Two sp^2 hybridised orbitals of each of the six carbons are used to form six C-C sigma bonds by inter nuclear axis overlapping of orbitals. The third sp^2 hybrid orbital of each carbon again undergoes internuclear axis overlapping but with the 1s orbital of hydrogen atoms to form six C-H sigma bonds when the molecule takes the shape of a regular hexagan with each carbon atom having one electron in the p orbital which is perpendicular to the C-C sigma bonds as shown below in Fig. 1 and 2. Electron cloud of this electron may be above and below the plane of C-C sigma bonds.
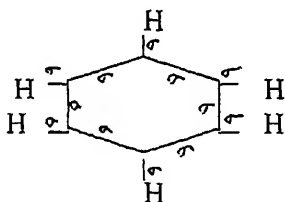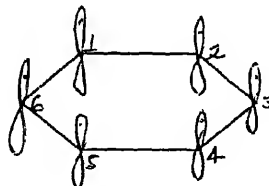
Fig.1   Fig.2

Bond length data indicates that all the six carbon – carbon bond lengths in benzene are the same. They are of the order of 139 pm which corresponds neither to carbon – carbon single bond nor to carbon – carbon double bond rather lying somewhere between the two bond distances. Bond distances being equal, electron of p orbital of each carbon has the equal tendency to undergo lateral overlapping with the two neighbouring carbon

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atoms thus not restricting the π electron cloud in any one position rather allowing to spread in both the directions. This is known as delocalisation of π electrons. That is electron of p orbital of C_1 can undergo lateral overlapping with the p orbital electron of C_6 on left hand side or C_2 on right hand side thus accounting for kekule's structures of benzene as shown in figs. 3-8.
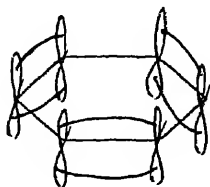
Fig.3   Fig.4 Kekule's structure (I)
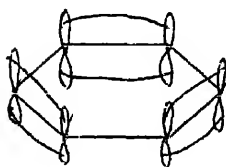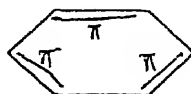
Fig.5   Fig.6 Kekule's structure (II)
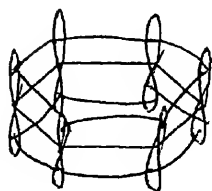
Fig.7   Fig.8

Thus there is delocalisation of all the six π electrons in the cyclic conjugated system of benzene. According to Hückel rule of aromaticity, there should be 6 π electrons (4x1+2) in benzene for aromaticity and there are actually 6 π delocalised electrons in benzene. Hence, benzene is an

aromatic compound. This number of 6 π delocalised electrons is known as aromatic sextet.

ii) Naphthalene

Naphthalene molecule consists of two benzene rings fused together in which there is delocalisation of 10π electrons (only one of the resonating structure is shown). Hence, naphthalene is also aromatic since the number of delocalised π electrons is as per Hückel rule.
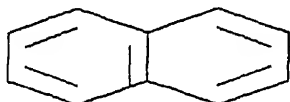
Naphthalene (Aromatic)

n=2   (πes: 4x2+2=10)

iii) Anthracene and Phenanthrene

Anthracene and phenanthrene consist of three benzene molecules fused together. Both possess 14π electrons. Value of n if taken as three, satisfies the Huckel rule (4x3+2=14). Since anthracene and phenanthrene molecules possess 14 π electrons as shown in one of their structures, they are also aromatic in nature.

Anthracene (Aromatic)   Phenanthrene (Aromatic)
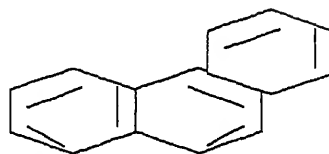
n=3 (πes:4x3+2=14)

Non-Benzenenoid compounds

i) **Azulene($C_{10}H_8$)**

Azulene consists of one cycloheptane ring and one cyclopentane ring fused together with alternate double and single bonds. Assuming n as 2, it should have 4x2+2 i.e. 10π electrons. It does possess 10π electrons in the cyclic system which can undergo delocalisation of π electrons. Hence, azulene is also aromatic in nature. It does not contain any benzene ring. Azulene is the example of non-benzenoid aromatic compound.:
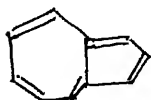
Azulene (Aromatic)

n=2 (π es: 4x2+2\10)

ii) **Cycloalkadienes**

Cycloputadiene and cyclopentadiene contain four π electrons i.e. they do not possess(4n+2) π electrons rather they contain 4n electrons. They are found to lack aromaticity. Cyclooctatetraene, containing four double bonds is found to be an unstable compound showing a high order of olefinic reactivity. Cyclobutadiene, cyclopentadiene, cyclohexadiene and cyclooctatetraene are found to be less stable than their acyclic (open chain analogues). They are called anti-aromtic compounds.
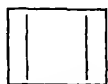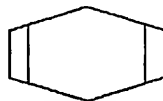
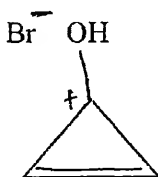| Cyclobutadiene	Cyclopentadiene	Cyclohexadiene	Cyclooctatriene
(4πes)	(4πes)	(4πes)	(8πes)
n :1	1	1	2

iii) Cyclic anions, cations and their salts

Cyclopropenyl cation(I) possesses 2π electrons which is in accordance with the Huckel rule (n=o). Cyclopropenyl cation is found to be a stable system. There is mention of its stable salts like hydroxycyclo propenylbromide and cyclopropenylhexachloroantimonate. They are aromatic in nature.
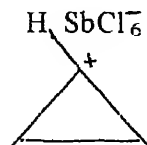

Cyclopropenyl cation	Hydroxy cyclopropenylbromide	Cyclopropenyl
	n=0 (πes:2)	hexachloroantimonate
(Aromatic)	(Aromatic)	(Aromatic)

I

Similarly cyclopentadienyl anion (II) satisfies the Huckel rule. It has a cyclic structure with delocalised six π electrons accounting for its aromatic character. Potassium salt of cyclopentadienyl cation and iron salt of dicyclopentadienyl cation, called ferrocene are found to be highly stable salts. Ferrocene is an orange solid (m.p.193°C) and found to show aromatic behaviour like benzene. Ferrocene $[(C_5H_5)-]_2Fe^{2+}$ undergoes acetylation and sulphonation reactions (S_E) which are characteristics of aromatic compounds. Structure of cyclopentadienyl anion II, its resonating structures and salts are given below

Cyclopentadienyl anion   Resonating structures of II

(II)

K+

(III) Potassium salt of
Cyclopentadienyl anion

Fe^{2+}
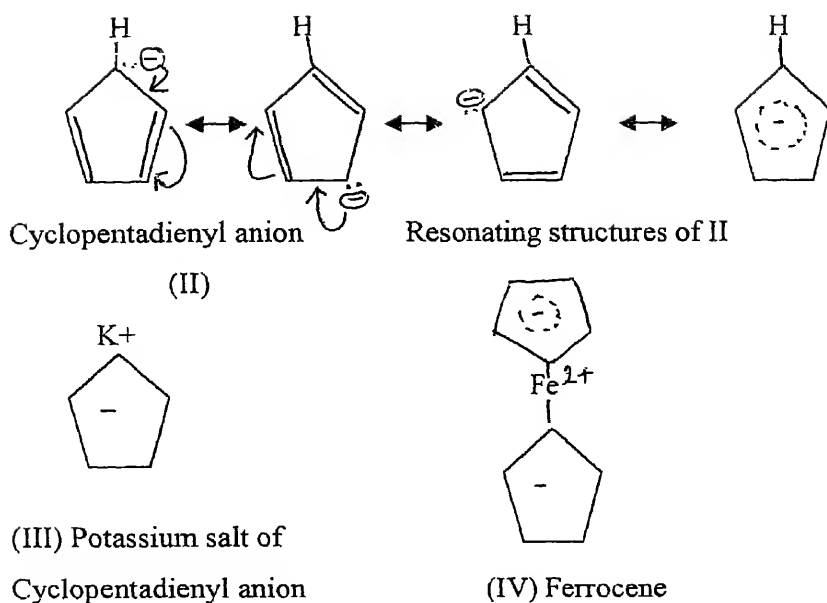
(IV) Ferrocene

Ferrocene isolated in 1951 is an example of non-benzenoid aromatic complex in which π es of cyclopentadienyl anion form a complex with Fe^{2+} ion thus leading to a revolution in the field of organic complexes of transition metals (Morrison, 2001).
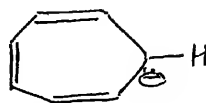
Cyclopropenyl and cycloheptatrienyl anions obtained by the loss of a proton from cyclopropene and cyclohepatriene possess 4 and 8 π electrons respectively which can undergo resonance. As they donot conform to $4n +2\pi$ electron rule of Hückel, they also fall in the category of anti aromatic ions. On the other hand, cycloheptatrienyl cation obtained by the loss of a hydride ion from cycloheptatriene is found to be highly stable and aromatic cation since this cation possesses only 6 π electrons (4x1+2) as per Huckel rule. Cyclopehtatrienyl cation is popularly known as a trophylium ion and its bromide salt trophylium bromide (C_7H_7Br) is a highly stable aromatic sold

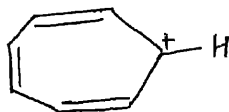with m.p.200°C. Number of π electrons present in these ions are shown in their structures given below.
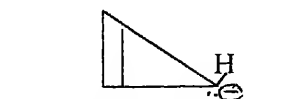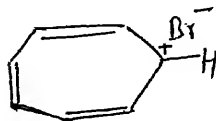

Cyclopropenyl anion
4πes (Anti-aromatic)

Cycloheptatrienyl anion
8πes (Anti-aromatic)

Cycloheptatrieny cation
6πes (Aromatic)

Cycloheptatrieny bromide
6πes (Aromatic)

(iv)   Heterocyclic compounds

Pyrrole, furan, thiophene, pyridine etc. are also the examples of non benzenoid compounds. Except pyridine, all of them contain 4 π electrons due to the presence of two double bonds but all of them fall in the category of aromatic compounds since the lone pair of electrons present on the hetro atom in pyrrole, furan and thiophene participates in delocalisation of π electrons.

Thus all these non benzenoid compounds can be considered as consisting of 6 π electrons conforming to the Hückel rule (taking n=1) and are found to show aromatic behaviour. Delocalisation of cyclic π electrons including the

lone pair of electrons on nitrogen atom in pyrrole is shown below for illustration :
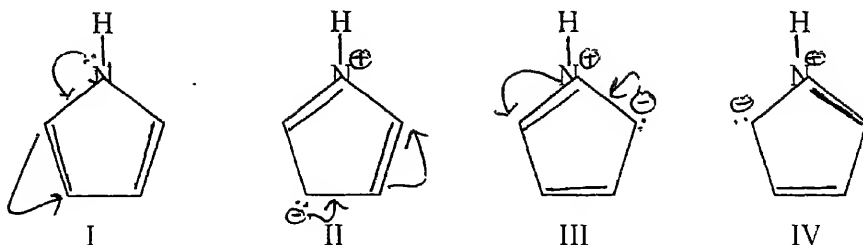
Thus it is very clear that the lone pair of electrons present on nitrogen atom also participates in delocalisation. Hence, the cyclic π electrons undergoing resonance in pyrrole are 6 instead of 4 as appears in its structure. For n=1, there should be 6 π electrons i.e. why pyrrole resembles benzene in aromatic behaviour. Same is the case with furan and thyophene. However, in case of pyridine(C_5H_5N) , lone pair present on nitrogen does not participate in delocalisation of π es, otherwise nitrogen will become tetravalent which is not possible. Excluding the lone pair of electrons on nitrogen atom, pyridine is also found to possess 6 π electrons for n=1 and thus accounting for its aromatic character.

v) Annulenes

Annulenes are monocyclic conjugated polyenes containing ten or more carbon atoms. They are named by putting the total number of carbon atoms in square brackets followed by annulene. Structures of [14] annulene and [18] annulene are given below :

[14] Annulene   [18] Annulene
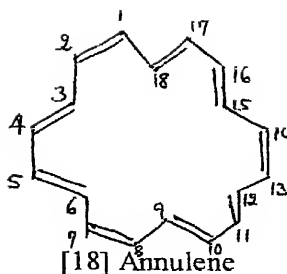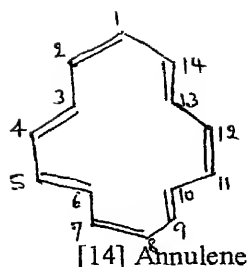
[14] annulene possesses 14 π electrons (4x3+2) and [18] annulene possesses 18 π electrons (4x4x2) as per Hückel rule and thus both are aromatic in nature.

4.Aromaticity in terms of π es energy

Terms aromatic, non-aromatic and anti aromatic are also in use (Jain.2001). These are described in terms of π electrons energy of the cyclic structure as compared to the corresponding open chain counterpart as given below in the box.

(i)   For aromatic compounds

π es enegy of the cyclic structure < π es energy of corresponding acyclic structure

Example

π es energy of Benzene < π es energy of 1,3,5 Hexatriene.

(ii)For non-aromatic compounds

π energy of the cyclic structure = π es energy of corresponding acyclic structure

Example : π es energy of [30] annulenes = πes energy of the corresponding acyclic structure

iv)   For anti-aromatic compounds

π energy of the cyclic structure > π es energy of correspond acyclic structure

Example

πes Energy of cyclobutadiene etc > π es energy of 1,3 butadiene etc

CHEMICAL KINETICS

Dr. Charanjit Kaur

Chemical Kinetics deals with the rate of change from initial to final state under non equilibrium conditions.

Besides offering useful rate equations to describe the speeds of chemical reactions, chemical kinetics attempts to describe exactly how each reaction occurs. The ultimate goal of chemical kinetics is a theory interrelating energies, structures, time for the single chemical events.

Slow and Fast Reactions →

(a)   Slow Reactions →   which proceed slowly and their rates can be measured by conventional methods. e.g. Inversion of cane sugar in aqueens solution

$$C_{12}H_{22}O_{11}+H_{2)}O \quad \rightarrow \quad C_6H_{12}O_6+C_6H_{12}O_6$$
Cane sugar   glucose   fructose

In these reactions a large no. of bonds are to be broken and a large no. of bonds have to be formed.

b)   · Fast Reactions →   The rates of many reactions are too fast to be measured by the conventional methods. The rates of fast reactions can be measured by employing special methods. Typical examples are –

(i)   ionic reactions such as neutralizations of acids by bases.
(ii)   Reactions of biological significance
(iii)   Organic substitution reactions
(iv)   The explosive reactions of O_2 with H_2 and hydrocarbon

Rate of Reaction → Rate of reaction is defined as the "Rate of change of concentration of either reactant or product per unit time."

$$R = dx/dt = - dc_{A/dt} = KC_A$$

Where dc_A denotes the infinitesimally small decrease in concentration of A in an infinitesimally interval of time dt. C_A denotes the concentration of reactant A at the given instant and K denotes the rate constant of a reaction.

Unit – The unit of rate is reaction is expressed in gm moles per litre per unit time (written as $mole^{-1} litre^{-1} time^{-1}$)The time in minutes or seconds.

Factors Affecting Reaction Rates.

(i) The nature of the reacting species fast reactions $NaOH + HCl \rightarrow NaCl + H_2O$ slow reactions $N_2 + 3H_2 \rightleftharpoons 2NH_3$.

(ii) Concentration of reactions $\rightarrow$ Rate is governed by the law of Mass Action. Rate concentration of reactants.

(iii) Effect of temperature $\rightarrow$ Rate of reaction $\propto$ temperature.

The rates of many reactions are approximately doubled or tripled for $10°C$ rise in temperature.

Temperature coefficient $= \dfrac{K_1 + 10}{K_1}$

Its value lies generally between 2 and 3.

Temperature rise $\rightarrow$ heat energy $\rightarrow$ K-E of the reacting molecules $\rightarrow$ number of collisions $\xrightarrow{\hspace{2cm}}$ increases the rate of reaction.

(iv) Effect of the presence of a catalyst

The rates of certain reactions may be increased by the presence of certain substances in the reacting system. These substances have been termed catalyst e.g.
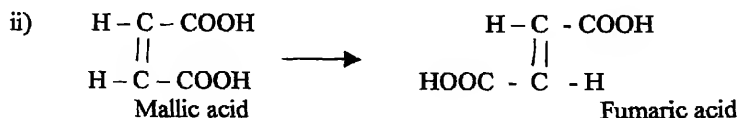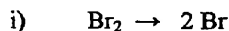
$$2KClO_3 \xrightarrow{[MnO_2]} 2KCl + 3O_2$$
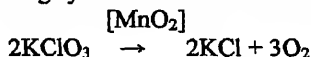
(v) Particle size in heterogeneous reactions or exposed area $\rightarrow$

Rate of reaction $\propto$ Surface area
Subdivision increases the surface area

(vi) Effect of radiation $\rightarrow$ Energy derived from X-rays, UV rays, visible, IR rays, radiowaves also affect the rate of reaction.
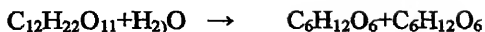
Molecularity of a Reaction $\rightarrow$ It is the sum of the number of molecules of various reactants that take part in a chemical reaction as represented by a balanced chemical equation. Classification is as follows.
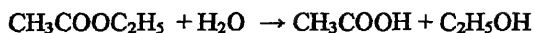
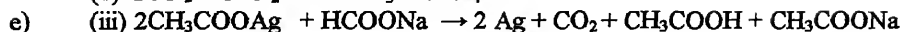a) Unimolecular Reactions $\rightarrow$

    i) $Br_2 \rightarrow 2\,Br$

    ii)

$$\begin{array}{l} H - C - COOH \\ \quad\ \, || \\ H - C - COOH \\ \quad\text{Mallic acid} \end{array} \longrightarrow \begin{array}{l} H - C\ \text{-}\ COOH \\ \quad\ \, || \\ HOOC\ \text{-}\ C\ \text{-}\ H \\ \qquad\qquad\text{Fumaric acid} \end{array}$$

b)   Bimolecular Reactions →

    (i)   Inversion of cane sugar

        $C_{12}H_{22}O_{11}+H_2O$ → $C_6H_{12}O_6+C_6H_{12}O_6$

    (ii)   hydrolysis of an ester –

        $CH_3COOC_2H_5 + H_2O$ → $CH_3COOH + C_2H_5OH$

c)   Termolecular Reaction →

d)   (i) $2NO + O_2$ → NO_2
    (ii)$2FeCl_2 + SnCl_2$ → $2FeCl_3 + SnCl_4$
e)   (iii) $2CH_3COOAg + HCOONa$ → $2\ Ag + CO_2 + CH_3COOH + CH_3COONa$
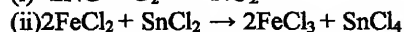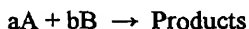
Order of a Reaction →

The order of a reaction is given by the number of atoms or molecules whose concentration alter during the chemical change
Consider a reaction of the type –

    $aA + bB$ → Products
The rate of reaction $\propto C_A{}^a \times C_B{}^b = KC_A{}^a \times C_B{}^b$

Then the order of reaction = a+b. Therefore, the order of the reaction may be defined as –

The sum of powers to which the concentration (or pressure) terms are raised in order to determine the rate of the reaction". The various differences between order and molecularity of a reaction are given below.

Order of a reaction	Molecularity of a reaction
1. It is experimentally determined quantity, which is obtained from the rate of overall reaction.	1. It is theoretical concept which depends on the rate determining in the reaction mechanism.
2. It possess all sorts of values including zero.	2. It is generally not exceeding 3 and never Zero.
3. It may be whole number or fractional value.	3. It is always a whole number

4. It cannot be obtained from a balanced chemical equation.	4. It is obtained from a single balanced Chemical equation.
5. It does not reveal anything about the mechanism of the reaction	5. It reveals some basic facts about reaction mechanism.
6. It is equal to the sum of the exponents of the molar concentration of the reactants in the rate equation.	6. It is equal to the no. of molecules of the reactants which are taking part in a single step chemical reaction.

Kinetics of zero Order Reactions →

If the concentration of the reactants remains unaltered during the course of reaction, it is said to be of zero order.

$dx/dt = K_o$ (1) where x is the concentration of product formed and K_o is the rate constant for zero order reaction. On integrating eg. (1)
with respect to t, we get

$dx = K_o \ dt$ or $x = K_o t + constant - (2)$

since $x = O$ when $t = O$ $\quad O = K_o x \quad O + const.$ Or const. $= O$ .... (3)

comparing 2 & 3 we get $x = K_o t$ .... (4)

Kinetics of First Order Reactions → A → Products ....(1)

Suppose a is the initial concentration of A in g mole/L. Let x g moles/L of A decomposes in time t the rate of the reaction at time t is according to the law of Mass Action υe

$\dfrac{dx}{dt}$ (a-x) or $\dfrac{dx}{dt} = K_1(a-x)$ .... (2)

or $\dfrac{dx}{(a-x)} = K_1 \ dt$ On integrating this eq.

We get $- \ln (a-x) = K_1 t + C$ (constant for integration)---- (3)

When $t = O$ $x = O$ eq (3) becomes as $- \ln a = C$ ...(4)

Substituting eg (4) in (3), we get

$Ln \dfrac{a}{(a-x)} = K_1 t$ or $K_1 = \dfrac{1}{t} \ln \dfrac{a}{a-x}$
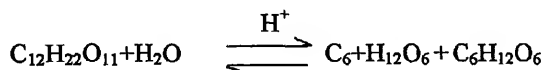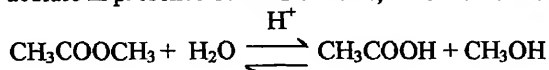
or $K_1 = \dfrac{2.303}{t} \log_{10} \dfrac{a}{(a-x)}$ [since ln x = 2.303 log$_{10}$x]

This is known as kinetic equation for the first order reaction.

Units $\rightarrow$ $K_1 = \dfrac{2.303}{t} \log \dfrac{a}{(a-x)} = $ time^{-1} log $\dfrac{mol/L}{mol/L}$

       $K_1 = $ time^{-1}

Pseudo unimolecular reactions $\rightarrow$ The reactions which are not unimolecular but follow the first order equation are said to be pseudo unimolecular reactions. e.g. Hydrolysis of methyl acetate in presence of mineral acids, Inversion of cane sugar etc.

$$CH_3COOCH_3 + H_2O \underset{\longleftarrow}{\overset{H^+}{\longrightarrow}} CH_3COOH + CH_3OH$$

$$C_{12}H_{22}O_{11} + H_2O \underset{\longleftarrow}{\overset{H^+}{\longrightarrow}} C_6 + H_{12}O_6 + C_6H_{12}O_6$$

Here the active mass of water is not changing appreciably in dilute solution.

Kinetics of Second Order Reactions $\rightarrow$

       $2A \rightarrow$ Products $-------$ (1)

       $dx/dt \propto (a-x)(a-x)$ or $\dfrac{dx}{dt} = K_2(a-x)^2$ .... (2)

on integrating eq. (2), we get

$\int \dfrac{dx}{(a-x)^2} = K_2\int dt$ or= $\int (a-x)^{-2} dx = K_2\int dt$ $(a-x)^2$

       $= \dfrac{(a-x)^{-2+1}}{-2+1} = Kt + C$ .... (3)

       $= -\dfrac{(a-x)^{-1}}{1} = kt + C$

or $\dfrac{1}{(a-x)} = Kt + C$ $--------$ (4)

When t = O   x = O   eq (4) takes the form

       $\dfrac{1}{a} = C$ $---------$ (5)

Comparing (4) & (5)   we get $\dfrac{1}{(a-x)} = Kt + \dfrac{1}{a}$

or $Kt = \dfrac{1}{(a-x)} - \dfrac{1}{a}$

$\dfrac{a-(a-x)}{(a-x)\,a} = \dfrac{x}{(a-x)a}$

$K = \dfrac{1}{ta} \quad \dfrac{x}{(a-x)}$ \hspace{2cm} ————————(6)

Units →

$K_2 = \dfrac{1}{Sec.} \quad . \quad \dfrac{moles/L}{moles/L \times moles/L}$

$= \dfrac{1}{sec.} \quad . \quad \dfrac{L}{moles} \quad = Litre/mole\ sec.$

$= L\ Mole^{-1}\ sec^{-1}$

Methods for determination of order of a reaction →

1) Graphical Method → The reaction velocity in a first order of reaction is determined by the variation of one concentration term, in the second order by the variation of two concentration terms and so on. Mathematically, it may be put as –

$dx/dt = K_1 (a.x)^1$ for the first order reaction
$dx/dt = K_2(a-x)^2$ for the second order reaction
$dx/dt = K_n (a-x)^n$ for the n^{th} order reaction.

If a curve is plotted between dx/dt and $(a-x)$, $(a-x)^2$, $(a-x)^n$ a straight line confirms the order.

Isolation Method → This method is due to Ostwald (1902). In this method, all the reactants except one are taken in large quantities so that concentrations remain constant throughout this change. Thus, the order of the reaction is determined with respect to the isolated reactant which is not taken in large quantity. The experiment is repeated by isolating each reactant in turn. The total order of the reaction will be given by the sum of the order of isolated reactions. This can be seen by the sum of the order of isolated reactions:

$N_1 A + n_2 B + n_3 C \rightarrow$ Products

Reaction velocity is given by –
$dx/dt = C_{An_1} C_{Bn_2} C_{cn_3}$

In the first experiment the reactants B and C are taken in large excess and the order of the reaction is to be determined with respect to A. Let this order be n_1 with respect to A.

In the second experiment, the reactants A & C are taken in large excess and the order of the reaction is to be determined with respect to B. Let this order be n_2. In the
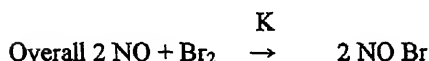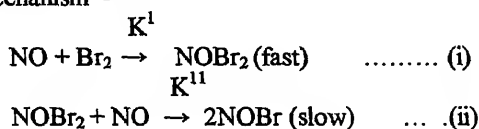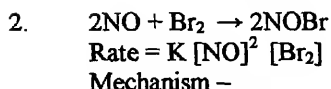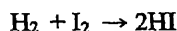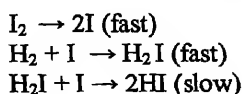

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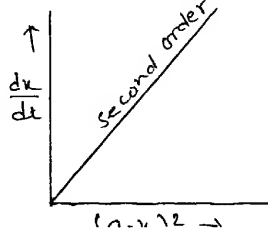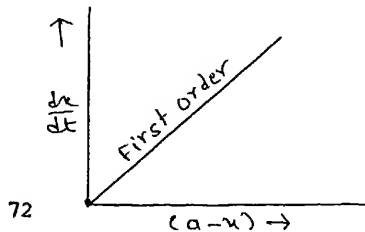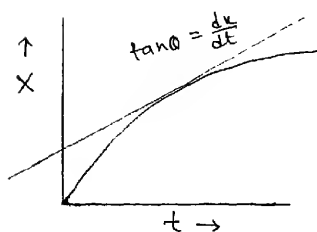
third experiment, the reactants A and B are taken in large excess and the order of this reaction is determined with respect to C. Let this order be n_3.

Total order of the reaction will be $n_1 + n_2 + n_3$ ie. Total order $= n_1 + n_2 + n_3$.

Mechanism of some Reactions –

1. $H_2 + I_2 \rightleftharpoons 2HI$
    Rate $= K \ [H_2] [I_2]$
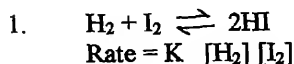
    But, the formation of HI has been explained on the basis of following mechanism

    $$I_2 \rightarrow 2I \text{ (fast)}$$
    $$H_2 + I \rightarrow H_2I \text{ (fast)}$$
    $$H_2I + I \rightarrow 2HI \text{ (slow)}$$
    _____

    $$H_2 + I_2 \rightarrow 2HI$$

2. $2NO + Br_2 \rightarrow 2NOBr$
    Rate $= K [NO]^2 [Br_2]$
    Mechanism –

    $$NO + Br_2 \xrightarrow{K^1} NOBr_2 \text{ (fast)} \quad \ldots\ldots\ldots \text{ (i)}$$
    $$NOBr_2 + NO \xrightarrow{K^{11}} 2NOBr \text{ (slow)} \quad \ldots \text{ .(ii)}$$

    Overall $2 NO + Br_2 \xrightarrow{K} 2 NO Br$

    The rate determining step involves 1 molecule of NO and 1 molecule of $NOBr_2$. Thus the expected rate expression should be

    Rate $= K^{11} [NOBr_2] [NO]$

However, $NOBr_2$ is a reaction intermediate and its concentration at the beginning of second step cannot be directly measured.
Concentration of $NOBr_2$ will be equal to –

$$[NOBr_2] = K^1 [K^1 [NO] [Br_2]$$

If this is substituted in the above equation, we get

$$\text{Rate} = K^1 K^{11} [NO]^2 [Br]$$
$$= K [NO]^2 [Br_2]$$

NUCLEAR CHEMISTRY

Dr. Charanjit Kaur

Natural Radioactivity – It is a process in which nuclei of certain elements undergo spontaneous disintegration without excitation by any external means emitting certain types of invisible radiations. The elements which emit these radiations are termed radioactive elements. The activity is not affected by external factors such as temperature, pressure, environment etc. Unstable nuclei attain stability through disintegration.

Radioactive disintegration follows First order reaction as one atom breaks down to give one or more new atoms.

$${}^{a}A \rightarrow B \quad$$ If to start with t = O, the no. of
(a-x)
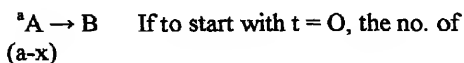
A present is a . After t seconds, x atoms will have decomposed leaving behind, (a-x) atoms. If then in a small time dt, dx is the no. of atoms which change, the rate of disintegration (dx/dt) can be expressed as –

$$dx/dt = K (a-x) - (1) \quad [\text{Law of Mass Action}]$$

Where K is ordinarily called velocity constant, and here it may well be named as disintegration constant or transformation constant.

From the expression (1) it follows –

$$\frac{dx}{(a-x)} = kdt \quad \text{-------- (2)} \quad \text{If dt} = 1 \text{ sec. K} = \quad dx$$

$$K = \frac{dx}{(a-x)}$$

Thus the Disintegration constant K may be defined as the fraction of the total no. of atoms $\frac{dx}{(a-x)}$ present at any time t which disintegrate per second. K has a definite characteristic value for a particular radioactive element.

$$\frac{dx}{(a-x)} = k \, dt \quad - \ln (a-x) = Kt + C \quad \ldots\ldots\ldots(3)$$
when t = O   x = O

eq. (3) takes the form - ln a = c   ....(4)

from 3 & 4
   -   ln (a-x) = Kt – lna

$$Kt = \ln a - \ln (a-x)$$

$$K = \frac{1}{t} \ln \frac{a}{(a-x)}$$

$$K = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} \qquad \text{---------- (5)}$$

Half – life period ($t_{1/2}$ or T)

Suppose, after time T, $x = a/2$, that is when half the atoms have disintegrated, the eq. (5) becomes –

$$K = \frac{2.303}{T} \log 2 \quad = \frac{0.693}{T}$$

$$\text{Or} \quad T = \frac{0.693}{K}$$

The time (T) required for the disappearance of one half of the original amount of radioactive substance is called its half life period.
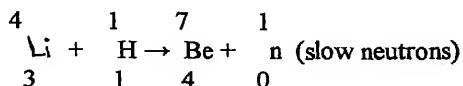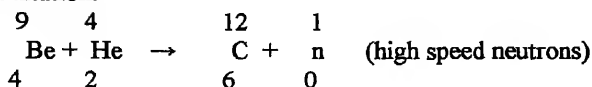
Artificial Transmutation →

Transmutation is defined as the conversion of one element into another or one type of atom into another. When this conversion is achieved by artificial means, it is termed as artificial transmutation.

Observation of Rutherford in 1919

$$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H$$
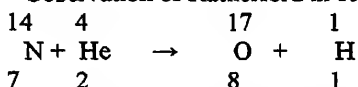
Later on, Rutherford and Chadwick showed that many other elements from B to K with the exception of C & Oxygen could be transmuted by bombardment with   particles. But to bring transmutation in heavier elements, the projectiles must have higher energies than α - particles obtained from natural sources. Gamow suggested proton (H) would be much more effective projectile than α- particle. Cyclotron of E.O. Lawrence was used to accelerate the speed of projectiles of 25000 miles per record.

The discovery of neutron by Chadwick in 1932 added another projectile for transmutation.

$$^{9}_{4}Be + ^{4}_{2}He \longrightarrow ^{12}_{6}C + ^{1}_{0}n \quad \text{(high speed neutrons)}$$

$$^{4}_{3}Li + ^{1}_{1}H \longrightarrow ^{7}_{4}Be + ^{1}_{0}n \text{ (slow neutrons)}$$
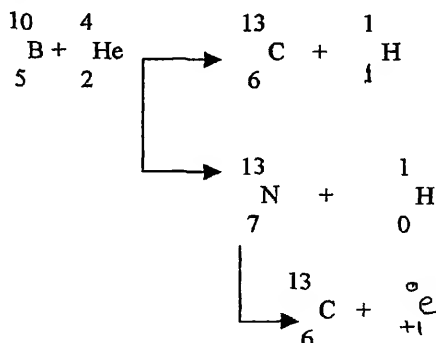
In general for the transmutation of lighter elements, charged particles like alpha particles, protons, deuterons are used while for heavier elements, neutrons are used.

Artificial Radioactivity → The process in which a stable isotope is converted into radioactive element by artificial transmutation is called artificial radioactivity.

When $^{27}_{13}Al$ is bombarded by α - particles, radioisotope $^{30}_{15}P$ is formed.

$$^{27}_{13}Al + {}^{4}_{2}He \longrightarrow {}^{30}_{141}Si + {}^{1}_{1}H \qquad \text{(95\% of total conversion)}$$

$$^{30}_{15}P + {}^{1}_{0}n \qquad \text{(5\% of total conversion)}$$

$$^{30}_{14}Si + {}^{0}_{1}e \qquad \text{Positron}$$
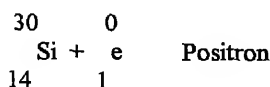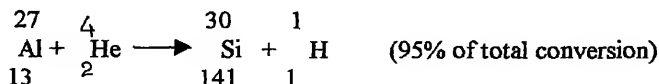
In a similar manner, the artificial radioactivity was observed when $^{10}_{5}B$ was bombarded by - particles

$$^{10}_{5}B + {}^{4}_{2}He \longrightarrow {}^{13}_{6}C + {}^{1}_{1}H$$

$$\longrightarrow {}^{13}_{7}N + {}^{1}_{0}H$$

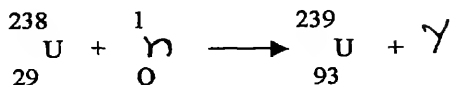$$\longrightarrow {}^{13}_{6}C + {}^{0}_{+1}e$$

Nuclear Reactions → The reactions in which nuclei of atoms interact with other nuclei or elementary particles such as alpha particle, proton, deutrons, neutron etc. resulting in the formation of a new nuclei and one or more elementary particles are called nuclear reactions e.g.
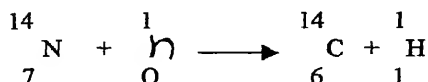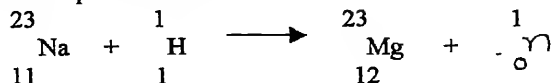
$$^{14}_{7}N + {}^{7}_{2}He \rightarrow {}^{17}_{7}O + {}^{1}_{1}H$$
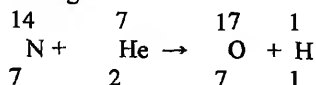
Types of Nuclear Reactions →

(a) Projectile capture reactions → The bombarding particle is absorbed with or without the emission of - radiations.

$$^{238}_{29}U + ^{1}_{0}n \longrightarrow ^{239}_{93}U + \gamma$$

(b) Particle – particle reactions →

$$^{23}_{11}Na + ^{1}_{1}H \longrightarrow ^{23}_{12}Mg + ^{1}_{0}n$$

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$$

(c) Spallation Reactions → High speed projectile with energies approximately 40 MeV may chip fragments from a heavy nucleus, leaving a smaller nucleus.

$$^{63}_{29}Cu + ^{4}_{2}He + 400\ MeV \longrightarrow ^{37}_{17}Cl + 14\ ^{1}_{1}H + 16\ ^{1}_{0}n$$
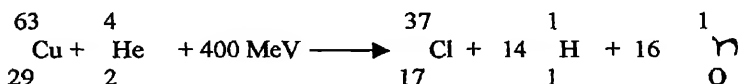
(d) Fusion Reactions → The process in which light nuclei are fused together to form heavy nuclei with the release of large amount energy is called nuclear fusion. E.g.

$$^{2}_{1}H + ^{2}_{1}H \longrightarrow ^{3}_{2}He + ^{1}_{0}n + E$$
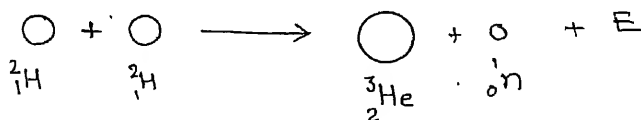
According to Bothe, 1939 the following reactions occur in the sun.

$$^{12}_{6}C + ^{1}_{1}H \longrightarrow ^{13}_{7}N + E$$

$$^{13}_{7}N \longrightarrow ^{13}_{6}C + ^{0}_{+1}e$$

$$^{13}_{6}C + ^{1}_{1}H \longrightarrow ^{14}_{7}N + E$$

$$^{14}_{7}N + ^{1}_{1}H \longrightarrow ^{15}_{8}O + E$$

$$^{15}_{8}O \longrightarrow ^{15}_{7}N + ^{0}_{+1}e$$

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$$^{15}_{7}N + ^{1}_{1}H \longrightarrow ^{12}_{6}C + ^{4}_{2}He$$

$$4\,^{1}_{1}H \longrightarrow ^{4}_{2}He + 2\,^{0}_{+1}e + 26.7\ MeV$$
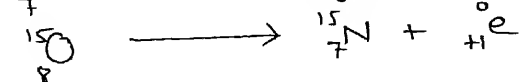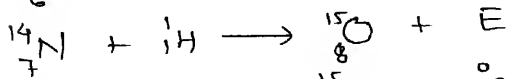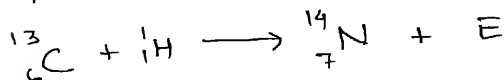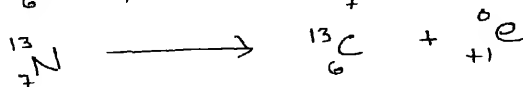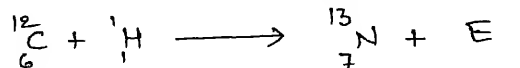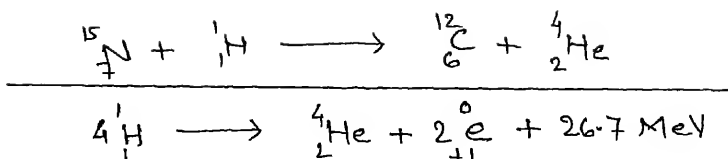
(e)   Fission Reactions → The process of artificial transmutation in which heavy nucleus is broken down into two higher nuclei of nearly comparable masses with release of large amount of energy is termed as nuclear fission e.g.

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{144}_{56}Ba + ^{90}_{36}Kr + 2\,^{1}_{0}n + E$$
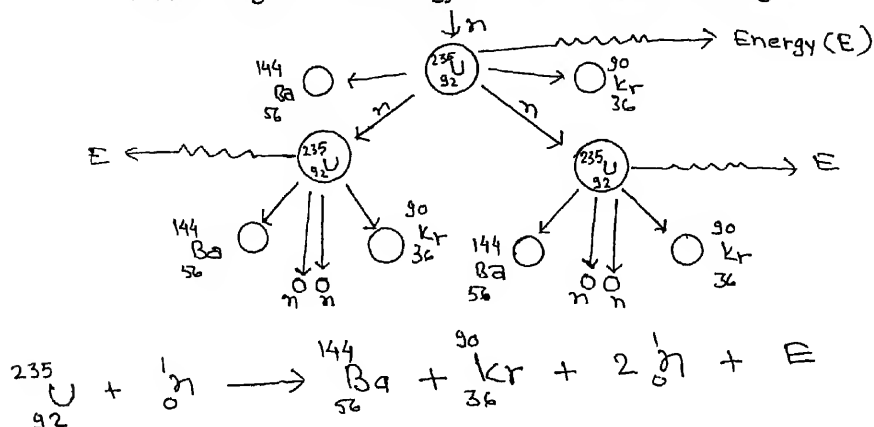
During fission, there is always loss of mass which is converted into energy according to Einstein equation $E = mc^2$. There is a loss of about 0.215 amu mass during one fission. This energy released in one fission is equal to 0.215x931 i.e. 200 MeV.

Nuclear Reactor → a nuclear reactor is a device for carrying out fission reducing at a controlled rate which enables the utilization of the released energy for peaceful purposes.

The number of neutrons resulting from a single fission is known as the multiplication factor when this is less than one, a chain reaction is not possible, when this factor is more than one a chain reaction might occur. In a nuclear reactor the fissionable material is so arranged that the multiplication factor is controlled to one. The nuclear reactors are of several types. The essential difference being the type and arrangement of fuel moderator and the mode of heat transfer unit. The following are the main parts of a typical nuclear reactor –

(A)   Reactor core   (i) Fuel   (ii) Moderator   (iii) Coolants

(iv)   Controlled Roads
(B)   Reflector   (c)   Pressure vessel   (D)   Shielding
(i)   Thermal shield   (ii)   biological shield (E) Heat Exchange   (F) Turbine

Nuclear Reactor or Atomic Pile
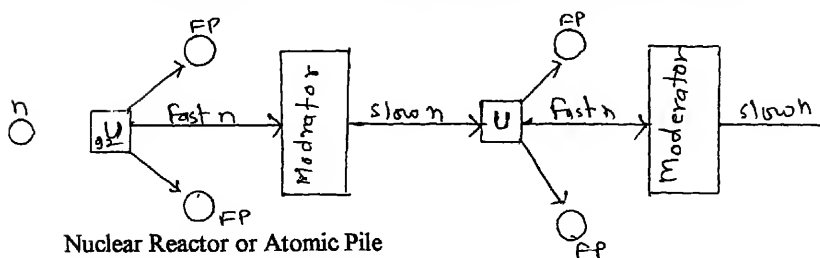
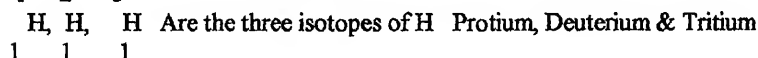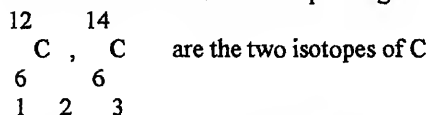It is evident that out of the 3 neutron one is absorbed by the moderator and lost. The second is absorbed by U^{238} to form Pu and the third splits up U^{235} and initiates the chain reaction. In India the first reactor "Apsara" was established at Bombay in 1952.

Isotopes $\rightarrow$

The atoms of an element which have same atomic number but different atomic masses or mass numbers are called Isotopes. E.g.

$$_6^{12}C \, , \, _6^{14}C \quad \text{are the two isotopes of C}$$

$$_1^1H, \, _1^2H, \, _1^3H \quad \text{Are the three isotopes of H Protium, Deuterium \& Tritium}$$

Radio carbon dating $\rightarrow$ By using half life period of $_6^{14}C$ it is possible to determine the age of various objects. In living materials the ratio of $_6^{14}C$ to $_6^{12}C$ remains relatively constant. When the tissue in an animal or plant dies, the $_6^{14}C$ decreases because the intake & utilization of C does not occur. Therefore, in dead tissues the ratio of ^{14}C to ^{12}C would decrease, depending on the age tissue. The age of the dead tissue is determined by burning the dead tissue & CO_2 is analysed for the ratio of ^{14}C to ^{12}C. From that data age of the dead tissue can then be confirmed.

ELECTROCHEMISTRY

Dr. Charanjit Kaur

Electrolysis → The process of chemical decomposition of an electrolyte by passage of electric current through it, is called electrolysis.

Cathode   NaCl   Anode

Na^+ Cl^-
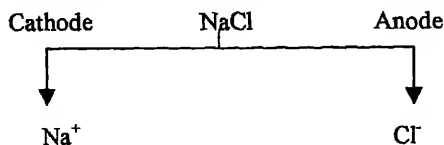
Faraday's Laws of Electrolysis →

(i) Faraday's First law → when an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electric charge passed through the electrolyte.

i.e. $W \propto Q$ W = mass of substance deposited
Q = Coulomb of charge

& $Q = I \times t$ (Current in amperes x time in sec.)

$W \propto I \times t$ or $W = Z \times I \times t$

Where Z = electro – chemical equivalent
If Q = 1 coulomb then W = Z

Thus, electro chemical equivalent can be defined as the mass of substance deposited by one coulomb of charge (one coulomb quantity of current)

(ii) Faraday's Second Law → when the same quantity of charge is passed through different electrolytes, then the masses of different substances deposited at the respective electrodes will be the ratio of their equivalent masses.

(iii) The law can be illustrated by passing same quantity of electric current through three voltameters containing solutions of H_2SO_4, $CuSO_4$, $AgNO_3$ respectively. In the first voltmeter, H_2 & O_2 will be liberated, in the second copper will be deposited and in the third, silver will be deposited.

H_2SO_4 $CuSO_4$ $AgNO_3$

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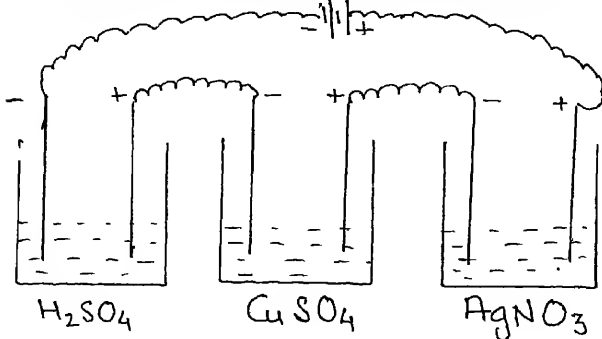
$$\frac{\text{Mass of hydrogen}}{\text{Mass of Copper}} \quad = \quad \frac{\text{Equivalent mass of hydrogen}}{\text{Equivalent mass of Copper}}$$

Or $\quad \dfrac{\text{Mass of Cu}}{\text{Mass of Ag}} \quad = \quad \dfrac{\text{Eq. Mass of Cu}}{\text{Eq. Mass of Ag}}$

For 1 coulomb

H_2 evolved	= 0.0000 1036 g
Cu deposited	= 0.0003292g
Ag deposited	= 0 001118g

From these masses, the amount of charge required to deposit one equivalent hydrogen or Cu or Ag can be calculated.

For hydrogen $= \dfrac{1}{0.00001036} = 96500$ coulombs

For Cu $= \dfrac{31.78}{0.0003292} = 96500$ coulombs

For Ag $= \dfrac{107.88}{0.001118} = 96500$ coulombs

This follows that 96500ncoullllombs of electric charge will deposit one of eq. of any substance. 96500 coulomb is termed as one Faraday and is denoted by F. Again from 1st law W = ZXQ.
When a = 96500 coulombs W becomes g. eq. Mass (E). ie $\quad$ E = Z x 96500

$$Z = \frac{E}{96500}$$

Conductance of Electrolytes : conductivity $= \dfrac{1}{\text{Resistance}} = \dfrac{1}{R}$

Specific conductance $\rightarrow$ Specific conductance is defined as the conductivity of one centimeter cube of the solution. It is represented by the symbol k, Kappa $\quad$ '

Reciprocal of specific resistance.

$k \quad = \quad \dfrac{1}{p} \quad = \quad \dfrac{1}{a} \text{ X } \dfrac{1}{R} \quad$ where P is specific resistance

Sp. Conductance is generally expressed in reciprocal ohms (r: O) or mhos or ohm^{-1}.

Equivalent Conductance (λ v)→ Equivalent conductance is the conductivity of all the ions produced by the dissociations of one g. equivalent mass of an electrolyte when dissolved in a certain volume ml

λ V = KxV where V is the volume containing 1g eq. of an electrolyte
Units = ohm^{-1} cm^2 equiv.$^{-1}$

Molecular conductance, μv
μV = KxV

Units = ohm^{-1} cm^2 mole^{-1}

Kohlrausch's law →
The equivalent conductivity at infinite dilution is for different electrolytes , the sum of two values, one depending upon the cation & the other on anion.

$\lambda\infty = \lambda a + \lambda c$

Applications of Kohlrausch's law →

(i) Calculation of Absolute Ionic Mobility,

(ii) Calculation of solubility of sparingly soluble salt → KV = $\lambda\infty = \lambda a + \lambda c$

(iii) Calculation of the Apparent degree of ionization, $= \dfrac{\lambda V}{\lambda\infty}$

(iv) Calculation of Ionic product of H$_2$O

λ H$_2$O   =   5.54x10^8 mhos
λ H$^+$ =   349.8 mhos
λ OH$^-$ =   198.5 mhos
λ (∞) H$_2$O   =   349.8+198.5 = 548.3 mhos

(H$^+$) = (OH$^-$)   = $\dfrac{5.5\text{x}10^8}{548.3}$ = 1.01x10^{-7}g ionL

Kw = [H$^+$] [OH] = 1.02x10^{-14} at 25°C.

(IV) Calculation   of degree of dissociation of weak electrolytes → For CH$_3$COOH take CH$_3$COONa, HCl & NaCl

(i) λ CH$_3$COO Na $= \lambda$ CH$_3$COO$^-$ $+ \lambda$ Na$^+$

(ii) λ HCl $= \lambda$ H$^+$ $+ \lambda$ Cl$^-$

(iii) λ NaCl $= \lambda$ Na$^+$ λ Cl$^-$

Add (i) + (ii) and substract (iii)

We get, λ CH$_3$COO $= \lambda$ CH$_3$COO Na $+$ λ HCl - λ NaCl.
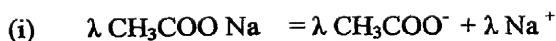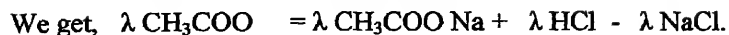
Galvanic or Voltaic cells.

It is a device in which chemical energy is converted into electrical energy. Here electricity is generated due to redox reaction going on in the cell. Daniel cell is the example of the Galvanic cell. At anode oxidation takes and at cathode reduction takes place.

$$Zn + Cu^{+2} \rightarrow Cu + Zn^{+2}$$

$\qquad\downarrow\qquad\qquad\quad\downarrow$

Anode   Cathode
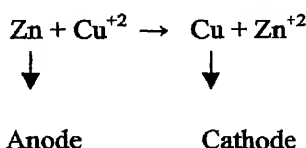
Electrode Potential $\rightarrow$ when a metal is placed in a solution of its ions, the metal acquires a +ve or –ve charge with respect to the solution. On account of this, a definite potential difference is developed between metal and the solution this potential difference is called **electrode potential.**

The magnitude of electrode potential of a metal is a measure of its relative tendency to lose or gain e$^-$. The magnitude of potential depends on the following factors:-

(i) Nature of the electrode

(ii) Concentration of the ions in solution

(iii) Temperature

Electrode potential may be

a) Oxidation Potential or b) Reduction Potential

E.M.F. of a cell → The difference of potential between two electrodes which causes flow of electric current from one electrode at a higher potential to another electrode at a lower potential is called electromotive force or E.M.F. of the cell.

$E° = E°$ right - $E°$ left

Nernst's equation → The electrode potential and the emf of the cell depends on the nature of the electrode, temperature and the activities (concentrations) of the ions in solution. The variation of electrode and cell potentials with concentration of ions in solution can be obtained from thermodynamic considerations. For a general reaction such as:- $m_1 A + m_2 B + \rightleftharpoons n_1 x + n_2 Y +$ (i) occurring in the cell, the Gibbs free energy change is given by the equation –

$$\Delta G = \Delta G° + 2.303RT \log_{10} \frac{a_x^{n_1} a_y^{n_2}}{a_A^{m_1} a_B^{m_2}} \quad \text{..........(ii)}$$

where a represents the activities of reactants and products under a given set of conditions and $\Delta G°$ refers to free energy change for the reaction when the various reactants and products are present at standard conditions. The free energy change of a cell reaction is related to the electrical work that can be obtained from the cell i.e. $\Delta G = - nFE$ cell and . $\Delta G° = - nFE°$ cell . On substituting these values in eq. (ii)

$$- \quad nFE \text{ cell} = - nFE° \text{ cell} + 2.303 \ RT \log_{10} \frac{a_x^{n_1} a_y^{n_2}}{a_A^{m_1} a_B^{m_2}} \quad \text{.....(iii)}$$

$$\text{or } E \text{ cell} = E° - \frac{2.303}{nF} \ RT \log_{10} \frac{a_x^{n_1} a_y^{n_2}}{a_A^{m_1} a_B^{m_2}} \quad \text{...............(iv)}$$

This is known as Nernnst equation.

Putting the values of $R = 8.314 \ JK^{-1} mol^{-1}$

$T = 25°C = 298K$ and $F = 96500C$, the eq. (IV) reduces to

$$E = E° - \frac{0.0591}{n} \log_{10} \frac{a_x^{n_1} a_y^{n_2}}{a_A^{m_1} a_B^{m_2}}$$

$$= E° - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

Primary Voltaic Cell (The Dry Cell):

In this cell, once the chemicals have been consumed, further reaction is not possible. It cannot be regenerated by reversing the current flow through the cell using an external direct current source of electrical energy. The most common example of this type is dry cell

The container of the dry cell is made up of Zn which also serves as one of the electrodes. The other electrode is a carbon rod in the center of the cell. The Zn container is lined with a porous paper. A moist mixture of NH_4Cl, MnO_2, $ZnCl_2$ and a porous inert filler occupy the space between the paper lined Zn container and carbon rod. The cell is sealed with a material like wax.

As the cell operates, the Zn is oxidized to Zn^{+2} i.e. $Zn \rightarrow Zn^{+2} + 2e^-$ (Anode). The e^- are utilized at C rod (cathode) as the NH_4^+ are reduced.

$$2NH_4^+ + 2e^- \rightarrow 2NH_3 + H_2$$
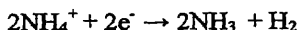
The cell reaction is –

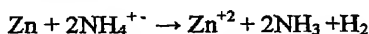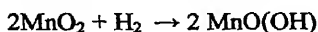$$Zn + 2NH_4^{+-} \rightarrow Zn^{+2} + 2NH_3 + H_2$$

H_2 is oxidized by MnO_2 in the cell

$$2MnO_2 + H_2 \rightarrow 2\ MnO(OH)$$

Ammonia produced at cathode combines with $Zn^{+2} + 4NH_3^- \rightarrow [Zn(NH_3)_4]^{2+}$

E cell is 1.6 volts.

Secondary Voltaic Cell (Lead storage Battery)　→ The cell in which original reactants are generated by passing direct current from external source i.e. it is re-charged, is called secondary cell. Lead storage Battery is the example of this type.

It consists of a group of lead plates bearing compressed spongy Lead, alternating with a group of Lead dioxide PbO_2,. These plates are immersed in a solution of about 30% H_2SO_4. When the cell discharges, it operates as a voltaic cell. The spongy lead is oxidized to Pb^{+2} and lead plates acquire a –ve charge.

$$Pb \rightarrow Pb^{+2} + 2e^- \ \text{(Anode)}$$
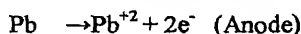
Pb^{+2} combine with SO_4^{-2} to form insoluble $PbSO_4$, which begins to coat lead electrodes.

$$Pb^{+2} + SO_4^{-2} \rightarrow PbSO_4 \ \text{(Precipitation)}$$

The e^- are utilized at PbO_2 (electrode)

$$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{+2} + 2H_2O \ \text{(cathode)}$$

$$Pb^{+2} + SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$$

Overall reaction is

$$Pb + PbO_2 + 4H^+ + 2\ SO_4^{-2} \rightarrow 2PbSO_4 + 2H_2O$$

E cell is 2.042 volts.

Recharging – $2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$
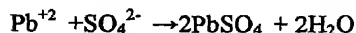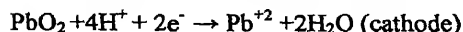
Fuel Cell → Fuel cells are another means by which chemical energy may be converted into electrical energy. The main disadvantage of a primary cell is that it can deliver current for short period only. This is due to the fact that the quantity of oxidizing agent and reducing agent is limited. But the energy can be obtained indefinitely from the fuel cell as long as the outside supply of fuel is maintained. One of the examples is the hydrogen oxygen fuel cell. The cell consists of 3 compartments separated by porous electrode. The hydrogen gas is introduced into one compartment and O_2 gas is fed into another compartment. These gases then diffuse slowly through the electrodes and react with an electrolyte that is in the central compartment. The electrodes are made of porous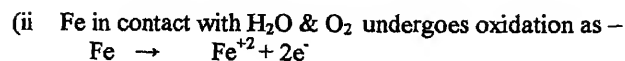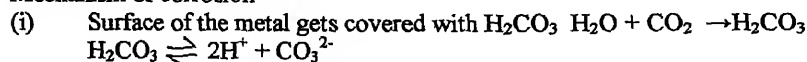 carbon and the electrolyte is a resin containing aq. NaOH solution. H_2 is oxidized at anode and O_2 is reduced at cathode. The overall call reaction produces water. The reactions which occur are –

Anode → $[H_2(g) + 2OH^-(aq) \rightarrow 2H_2O (l) + 2e^-] \times 2$

Cathode → $O_2(g) + 2H_2O (l) + 4e^- \rightarrow 4\ OH^- (aq)$

Overall $\quad 2H_2(g) + O_2 (g) + O_2 (g) \rightarrow 2H_2O(l)$
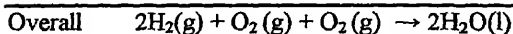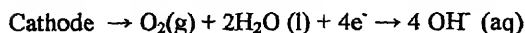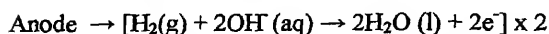
This type of cells are used in space crafts. Fuel cells are efficient and pollution free.

Corrosion ___The process of slowly eating away of the metal due to attack of the atomspheric gases on the surface of the metal resulting into the formation of compounds such as oxides, sulphides, carbonates, sulphates etc is called corrosion. Most common examples of corrosion is rusting of Iron. Rust is hydrated ferric oxide $Fe_2O_3\ xH_2O$. Some other examples include tarnishing of Ag, development of green coating on Cu and Bronze etc.

Mechanism of corrosion →
(i)   Surface of the metal gets covered with H_2CO_3 $H_2O + CO_2 \rightarrow H_2CO_3$
       $H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$

       $H_2O \rightleftharpoons H^+ + OH^-$

(ii   Fe in contact with H_2O & O_2 undergoes oxidation as –
       Fe → $Fe^{+2} + 2e^-$

       Thus the site where the above reaction takes place acts as anode.

(iii)The e^- lost by Fe is taken by H^+

$$H^+ + e^- \rightarrow H \qquad (4)$$
$$4H + O_2 \rightarrow 2H_2O \qquad \text{-------(5)}$$
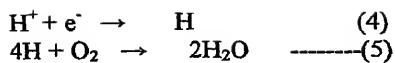
Multiplying eq. (4) by 4 and adding to 5 we get $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ .... (6) the dissolved O_2 may take up e^- directly to form OH $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

The sites where the above reaction takes place act as cathodes. Adding eg. (3) & (6) We get $2Fe + O_2 + 4H^+ \rightarrow 2Fe^{+2} + 2H_2O$.

It may be mentioned here that if H_2O is saline, it helps in the flow of current in a miniature cell and enhance the process of corrosion.

(iv) The Fe^{+2} formed reacts with dissolved O_2 from the air to form Fe_2O_3

$$4Fe^{+2} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+$$
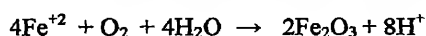
(v) Fe_2O_3 then undergoes hydration to form rust as follows –

$$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3\,xH_2O \text{ (rust)}.$$
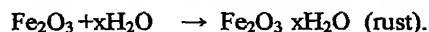
Prevention of corrosion

1. Barrier Protection

   a) Cover the surface with Paint

   b) Apply film of oil

   c) Coated with non corroding metal such as Ni, Cr, Al etc.

   d) Coated with chemicals

2. Sacrificial Protection –

   Example Galvanizing

3. Electrical Protection $\rightarrow$ More active metals like Mg, Zn, Al etc are deposited electrically over the surface to be protected from corrosion.

4. Using anti rust solutions $\rightarrow$ Alkaline phosphate and alkaline chromate solutions prevent corrosion. These are used in car radiators to prevent rusting of iron parts of the engine.

Nelson Cell

For NaOH & Cl₂

$$NaCl \rightarrow Na^+ + Cl^- \text{ Ionization}$$

$$Cl^- \rightarrow Cl + e-$$
$$Cl + Cl \rightarrow Cl_2 \quad\quad \text{at anode}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \text{at Cathode}$$

$$Na^+ + OH^- \rightarrow NaOH$$

88
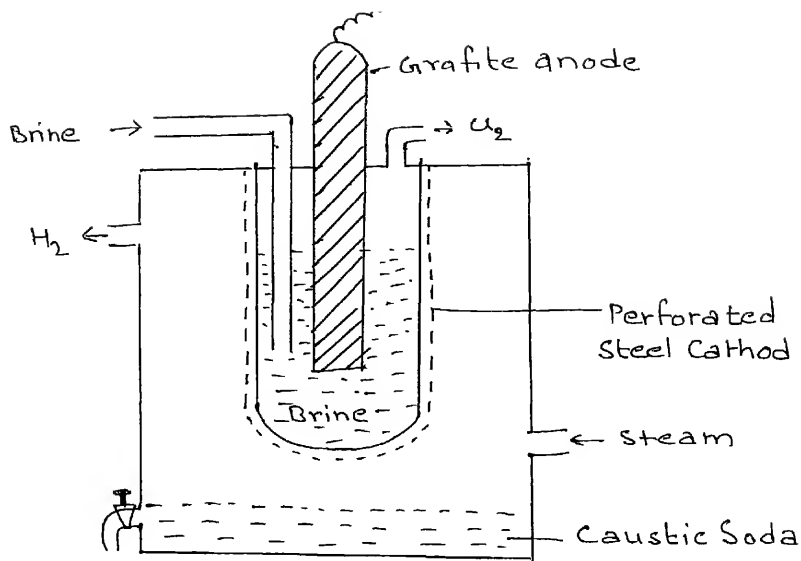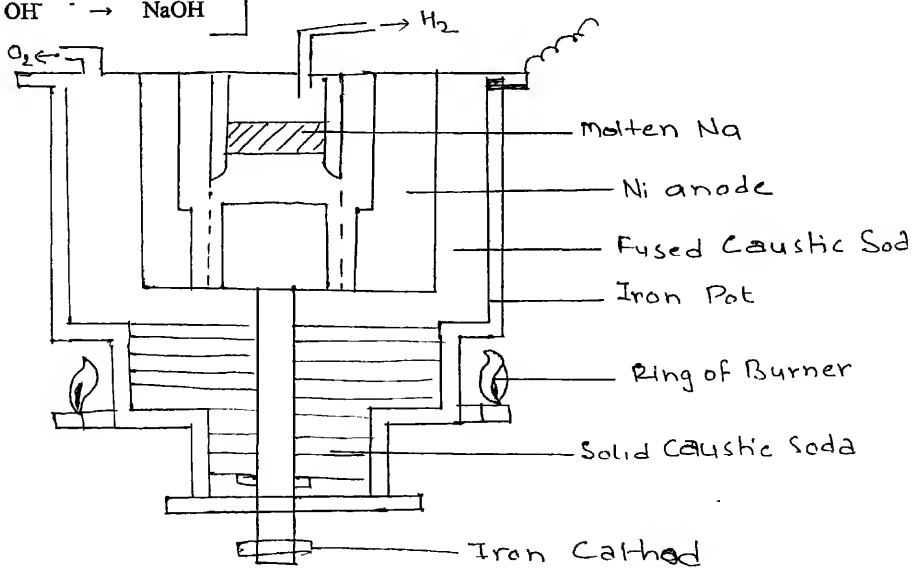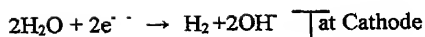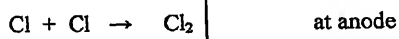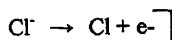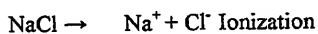
Castner's cell for the manufacture of Sodium.

Manufature of Na

$$NaOH \rightleftharpoons Na^+ + OH^-$$

$$Na^+ + e^- \longrightarrow Na \text{ (at Cathode)}$$

$$4OH^- \longrightarrow 2H_2O + O_2 + 4e^- \text{ (at anode)}$$
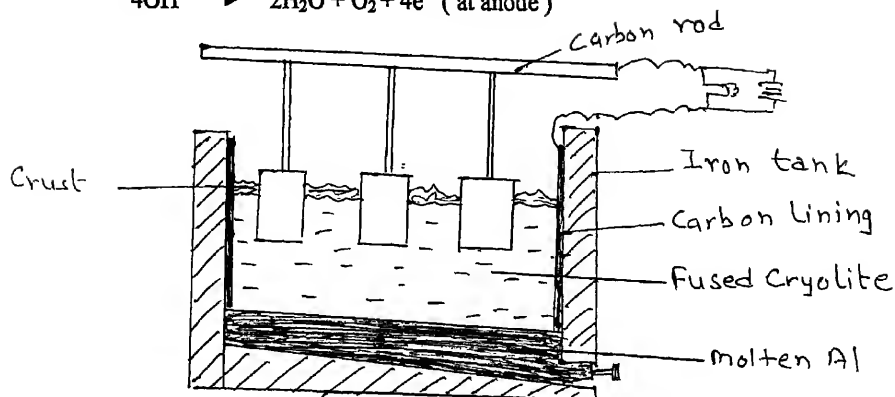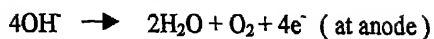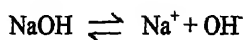
Electrolytic process for production of Al
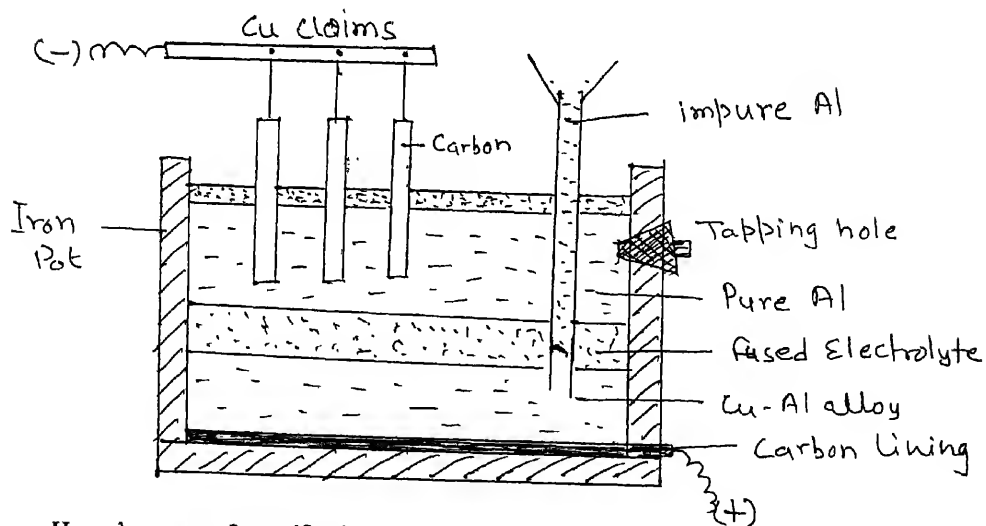
Hoope's process for purification of Al

Aluminium

Occurrence → in the combined state as silicates, oxides etc.

Most common are from which Al is profitably extracted is Bauxite which contains about 56% Al_2O_3 represented as Al_2O_3 $2H_2O$

Purification of Bauxite by
I.   a)   Hall's Process   b)   Baeyer's Process   c)   Serpeck's process
II.   Electrolytic reduction of alumina →
      Purified alumina is dissolved in molten mix. Of cryolite. An electric current of 5-6 volts and about 16000 – 9000 amperes is passed.

Following reactions take place –

$AlF_3 \rightarrow Al^{+3} + 3F^-$
$Al^{+3} + 3e^- \rightarrow Al$ at cathode
$3F^- \rightarrow 3F + 3e^-$

$Al_2O_3 + 12F \rightarrow 4 AlF_3 + 3O_2$

$4C + 3O_2 \rightarrow 2CO + 2CO_2$
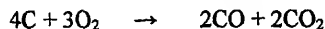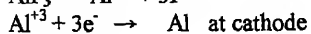
III.   Purification of Aluminium by Hoope's process

Electrolytic refining.
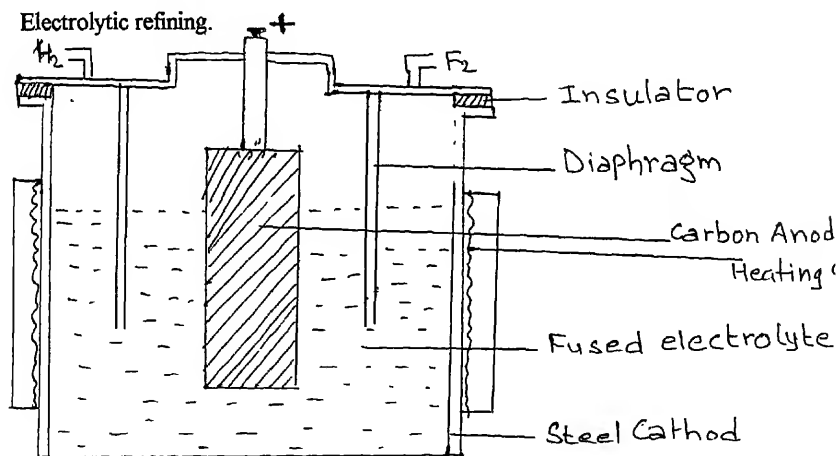
Modern Method for the manufacture of Fluorine

Electrolysis of $KHF_2 \rightarrow KF + HF$

$HF \rightleftharpoons H^+ + F^-$

$$2H^+ + 2e^- \longrightarrow \quad H_2 \text{ (At Cathode)}$$

$$2F^- - 2e^- \longrightarrow \quad Fe \text{ (At anode)}$$
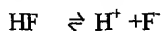
a current of 100-2000 amperes at 8.5 to 11 volts. A monel metal gauze is used for separating anode & cathode. F_2 obtained at anode is purified by passing through NaF

$$NaF + HF \longrightarrow \quad NaHF_2$$
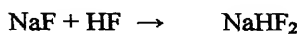
REPRESENTATIVE ELEMENTS-I

Dr. Sulekh C Agrawal

This includes s-block elements. s-block elements comprise two groups ie. 1 & 2. Group 1 consists Li, Na, K, Rb, Cs & Fr and commonly known alkali metals. Group 2 consists of Be, Mg, Ca, Sr & Ba and commonly known as alkaline earth elements. A comparative study has been made between alkali and alkaline earth metals.

(i) Electronic Configuration.

They has general outer electronic configuration ns^1 and ns^2 respectively.

Li [He]$2s^1$	Be[He] $2s^2$
Na[Ne]$3s^1$	Mg [Ne]$3s^2$
K[Ar]$4s^1$	Ca[Ar]$4s^2$
Rb[Kr]5s1	Sr[Kr]$5s^2$
Cs[Xe]$6s^1$	Ba[Xe]$6s^2$
Fr[Rn]$7s^1$	Ra[Rn]$7s^2$

Alkali metals after loosing one electron acquire noble gas electronic configuration. Therefore, to remove second electron is very difficult . They show only one valency. Alkaline earth metals can lose two electrons before for getting the noble gas electronic configuration. Therefore, they are bivalent.

1. Atomic Radii & Ionic Radii

Atomic and ionic radii increases from top to bottom in respective group.

I group (Li < Na < K < Rb < Cs , Fr)   II group (Be < Mg < Ca, < Sr < Ba < Ra)

It is due to increase in the number of shells. The radii decrease in the period from

left to right. So alkaline earth metals are smaller in size as compared to alkali metals.

2. M.P. & Hardness:

Alkaline earth metals are harder and show high melting points as compared to alkali metals. It is due to number of electrons used in bonding. Alkali metals utilize one electron whereas alkaline earth metals two. So metallic bonding in alkaline earth metals will be strong as compared to alkali metals.

3. I.P: Alkali metals show lowest value of I.P. because they are largest in size. However, due to small size alkaline earth metals show high value of I.P as compared to alkali metals.

3.   Colour

        Due to low value of I.P. electron can be easily excited from one energy state to other. All the alkali metals impart colour to the Bunsen flame.

Q. Why NaCl imparts colour inspite of both Na & Cl having noble gas electronic configuration ?

        The participants have been told that on heating the crystal it dissociates into atoms not ions. Therefore, it imparts colour.

        It has also been told to the participants that due to small size and high value of I.P. Be and Mg do not impart colour to the bunsen flame.

Reducing Properties:

        The reducing behaviour of alkali metals and alkaline earth metals has been discussed in detail. A question has been discussed why Li with high value of I.P. is a better reducing agent among the alkali metals ? This has been explained in terms of standard electrode potential. Due to high value of hydration energy in case of Li it shows more negative value of standard electrode potential.

        $Li \rightarrow Li^+(ag)$ $= -3.05$
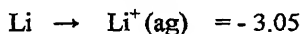
Trend of reducing properties is

        $Li(aq) > Cs > Rb > K > Na$
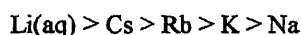
Then it has also been discussed, why Be being smaller than Li is not a better reducing agent? It has been explained in terms of higher I.P. of Be as compared to Li.

A number of other points have also been asked by participants.

1. Li forms oxide, Na peroxide whereas K superoxide also

2. Anomalous behavior of Li

3. Diagonal Relationship

4. Solubility of hydroxide and sulphates of alkaline earth metals

5. Stability of oxo salts of alkali and alkaline earth metals.

6. Solubility of Li halides.

REPRESENTATIVE ELEMENTS-II

Dr. Sulekh C. Agrawal

This includes p-block elements. This includes Group 13, 14, 15, 16, 17 and 18. The elements of these groups are important as fertilizers, Cement, paints and pigments. The general physical properties of these elements were explained to the participant.

Electronic configuration:

These groups of elements have general electronic configuration $ns^2 np^{1-6}$. The outer most electronic configurations are given below.

Group 13	14	15	16	17
$B2s^22p^1$	$C\ 2s^2 2p^2$	$N\ 2s^22p^3$	$O\ 2s^22p^4$	$F2s^2\ 2p^5$
$Al\ 3s^23p^1$	$Si\ 3s^23p^2$	$P\ 3s^23p^3$	$S\ 3s^23p^4$	$Cl3s^2\ 3p^5$
$Ga\ 4s^24p^1$	$Ge4s^24p^2$	$As4s^24p^3$	$Se4s^24p^4$	$Br4s^24p^5$
$In\ 5s^2\ 5p^1$	$Sn5s^25p^2$	$Sb5s^25p^3$	$Te5s5p^4$	$I5s^25p^5$
$Te\ 6s^26p^1$	$Pb6s^26p^2$	$Bi6s^26p^3$	$P_o\ 6s26p4$	$At6s^26p^5$

1. Atomic Radii:

The radii of these elements increase from top to bottom. However, the elements of 4^{th} periods are smaller as compared to elements of 3^{rd} periods. It is due to d-orbital contraction.

2. Metallic Character:

Metallic character increases from top to bottom. The first element is nonmetal, second may be mataloids and the last element shows metallic behavior. It is due to increase in electropositive character.

IP: Due to decrease in size the ionization potential increases from left to right. There are few exceptions.

For example: The first I.P. of nitrogen is higher as compound to oxygen because the nitrogen has 3 electrons in p-orbitals

$N = 2s^22p^3$

$O = 2s^22p^4$
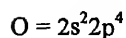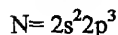
Since nitrogen is half filled , i.e. stable electronic configuration. A large amount of energy will be required to remove e^-, but in O after losing one electron from p-orbital it will have $3e^-$. So the removal of e^- is easier. If we compare the second I.P. than O has higher value than N because now O has $3e^-$ in p-orbital.

Electron Affinity:

Electron Affinity increases from left to right in a period and decreases in the group from top to bottom. However there are few exceptions.

For example

- The electron affinity of nitrogen group is almost zero. (Due to half filled np^3 stable electronic configuration.

- The electron affinity of group-18 elements is Zero because they have ns^2np^6 (completely filled p-orbital)

- The electron affinity of the first element of each group is lower than the second elements. For example electron affinity of F is lower than Cl. It is due to the small size of F. Due to this electron repulsion will takes place.

Electronegativity: It increases from left to right in periods and decreases in the groups from top to bottom. It is due to increase in size in the groups and decrease in size in periods.

Catenation:

Formation of chain type of compounds. It depends on the strength of A-A(atom-atom) bond. Among the p-block elements C has a maximum tendency to form chain type of compounds. It is due to a small size of carbon and strong metal-metal bond. If smaller size is the criteria for catenation that N O or F should show more catenation properties but it is not. Because there are lone pair present on N O or F. Due to lone pair of e^- repulsion takes place. Bond becomes weak.

Q.   C-C is stronger as compared to N – N but N = N is stronger as compared to C= C why ?

Inert pair effect:-

The reluctance of s-electron pair to take part in the formation of chemical bond is known as inert pair effect. It increases from top to bottom in the group.

For example Tl exists in +1 & +3 oxidation states. However +1 is the stable O.S. of Tl. Similarly we can explain the stability of +2 OS for Pb and +3 for Bi.

$$Tl = 6s^2 6p^1 \qquad Te^+ = 6S^2 6p^o$$

$$Pb = 6s^2 6p^2 \qquad Pb^{2+} = 6s^2 6p^o$$

$$Bi = 6s^2 6p^3 \qquad Bi^{3+} = 6s^2 6p^o$$
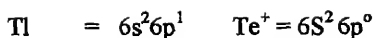
Group-13

Oxides:- All form oxides of the type M_2O_3. The oxide of B is acidic, Al_2O_3 is amphotence. Basic character increase from top to bottom.

Halides: All the halides are electron deficient. Boron forms BF_3 BCl^3 BBr_3 & BI_3.

Q :-Arrange these halides in increasing Lewis acid character.

Ans:- $BI_3 > BBr_3 > BCl_3 > BF_3$

Although on the basis of the polarity of bond BF_3 should have more Lewis acid character but it is least why. It can be explained as
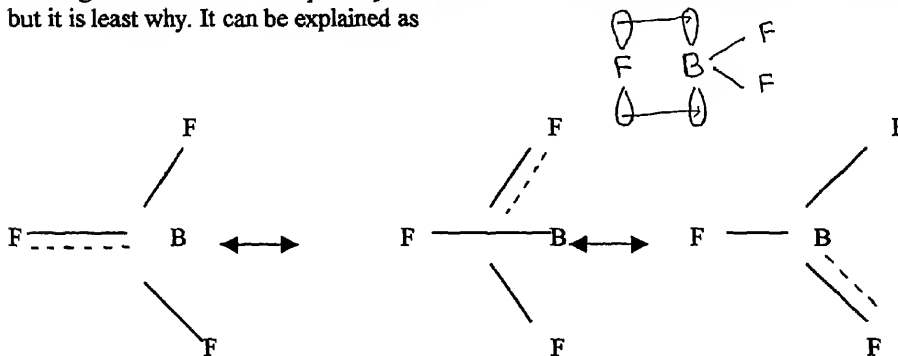
As a result of the backdonation of electrons from fluorine to boron, the electron deficiency of boron atom gets compensated and therefore, the Lewis acid character of BF_3 decreases. The tendency to form P_Π - P_Π bond is maximum in BF_3 and decrease rapidly as we move from BCl_3 to BI_3

Halides of other elements of group 13 also behave as Lewis acid. The Lewis acid strength decreases as B> Al> Ga> In.

Aluminium halides exist as dimeric

CL   Cl   Cl   Cl   Cl   Cl

$\diagdown$Al$\diagup$ + Al → $\diagup$Al$\diagdown$ Al$\diagup$

Cl$\diagup$ Cl   Cl   Cl   Cl   Cl
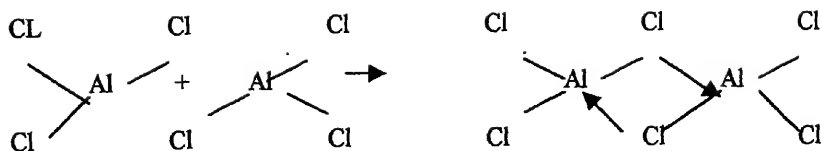
Structure of B_2H_6
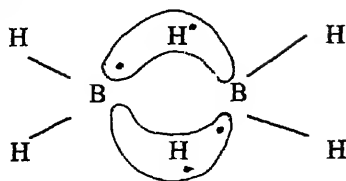
sp³ hybridization

_____

H_3BO_3: -

It is not an acid in protonic concept. However it is monobasic acid in Lewis acids base concept._

$$B(OH)_3 + H_2O \longrightarrow B(OH)_4^- + H^+$$

If the titration of H_3BO_3 VS NaOH is carried out then C_2H_5OH is required.

B(OH)₃+NaOH $\xrightarrow{C_2H_5OH}$
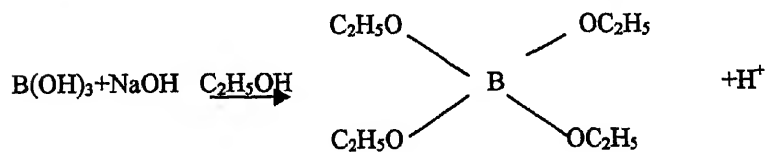
Basic character of oxide & hydroxides

B_2O_3	Al_2O_3	Ga_2O_3	In_2O_3	Tl_2O
$B(OH)_3$	$Al(OH)_3$	$Ga(OH)_3$	$In(OH)_3$	TlOH
Acidic				

Amphotenic   Basic

97

Group-14

Catenation: This is one of the remarkable properties of carbon. This property of forming bonds with the atoms of same element is called catenation.
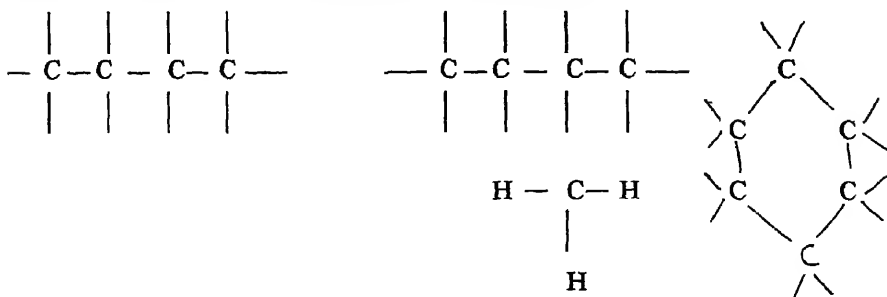
The tendency to catenation depends upon the strength of M-M bond

Bond energy (kJmol⁻¹)	C-C	Si-Si		Ge-Ge	Sn-Sn
	353.3	225.7		167.2	154.7
	C>Si	>	Ge	> Sn > Pb	

Carbon differs in properties to that of other elements in the same group.

1. Small Size
2. tendency to form P_Π-P_Π bonds (multiple bonds)
3. Absence of d-orbital

We can easily explain some questions related to carbon family.

(1) CO_2 is a gas whereas SiO_2 is solid

It is because multiple bond exists in CO_2

$O = C = O$ whereas Si forms only single bonds
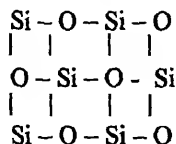
CCl_4 does not hydrolyse by water but $SiCl_4$ does.

It is due absence of d-orbital in C no water molecule will be able to attack on carbon but Si has 3d orbital.

$$Si(OH)_4$$
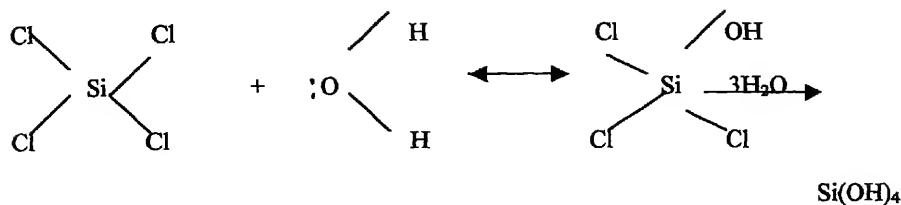
Group-15

Nitrogen is inert at room temperature due to $N \equiv N$ (high heat of dissociation 2e 945 Kjmol^{-1}. It shows less tendency of catenation due to presence of lone pair of electrons.

Hydrides   Bond angle
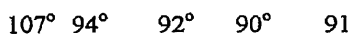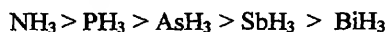
$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

107° 94°   92°   90°   91

Basic strength

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Thermal stability

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Reducing character

$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

Boiling point

$BiH_3 > SbH_3 > NH_3 > AsH_3 PH_3$
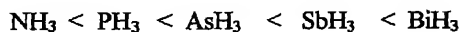
Structure of oxyacids of Phosphorous

H_3PO_2

$$\begin{array}{c} O \\ \| \\ P-H \\ \diagup \quad \diagdown \\ OH \quad \quad H \end{array}$$

H_3PO_3

$$\begin{array}{c} O \\ \| \\ P-H \\ \diagup \quad \diagdown \\ OH \quad OH \end{array}$$

H_3Po_4

$$\begin{array}{c} O \\ \| \\ P - OH \\ \diagup \quad \diagdown \\ OH \quad OH \end{array}$$

HPO_3

$$\begin{array}{c} O \\ \| \\ P \\ \diagup \quad \downarrow \\ OH \quad O \end{array}$$
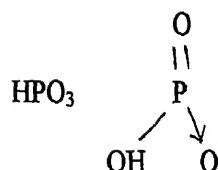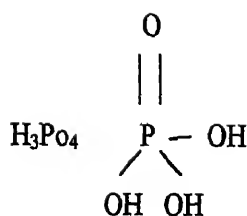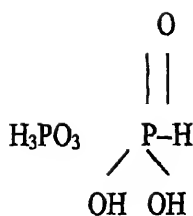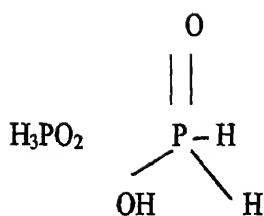
It is found in polymetric form

Metaphosphoric acid

Trimetaphospheric acid

Polymeta phosphoric acid

●

$$\begin{array}{c} O \quad O \\ \| \diagup \\ \quad P \quad \quad P = O \\ \diagup | \quad \quad | \diagdown \\ OH \quad O \quad \quad O \quad OH \\ \diagdown \quad \diagup \\ \quad P \\ \diagup \quad \backslash\backslash \\ OH \quad \quad O \end{array}$$

$$\begin{array}{cccc} O & O & O & O \\ \| & \| & \| & \| \\ P & P & P & P \\ \diagup \backslash \diagup & \diagup \backslash \diagup & \backslash \diagup & \backslash \\ O \quad | \quad O & | \quad O & | \quad O & | \\ OH & OH & OH & OH \end{array}$$
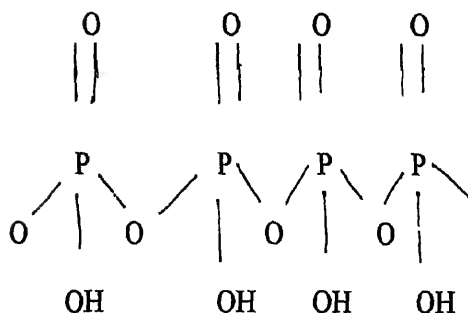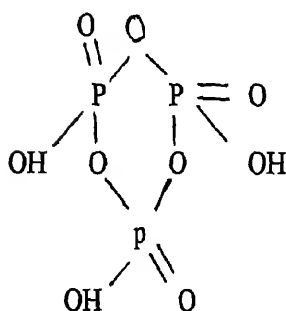
Group- 16 O_2 is also inert at room temperature. O_2 and S_2 are paramagnetic in nature.

Why O_2 is paramagnetic ? This can be explained on the basis of molecular orbital theory.

Structure of Oxyacids of Sulphur

H_2SO_3 H_2SO_4 $H_2S_2O_3$ $H_2S_2O_4$

$H_2S_2O_5$ $H_2S_2O_6$ $H_2S_2O_7$

H_2SO_5 $H_2S_2O_8$
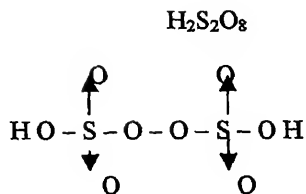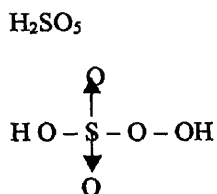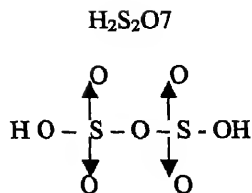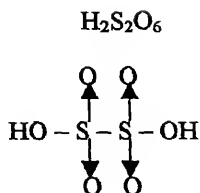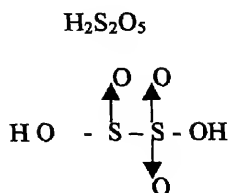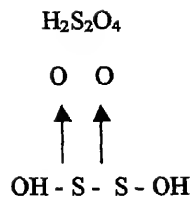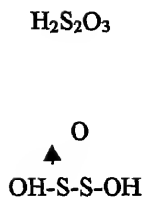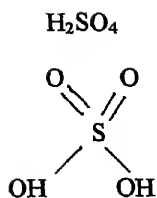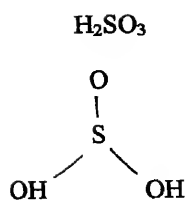
Halides

SF_6 is known but not SCl_6

It is due to large size of Cl.

Group-17

Chlorine has high electron affinity but F is a better oxidizing agent

$KF + Cl_2 \longrightarrow$ No Reaction

If we take

$KCl + F_2 \longrightarrow KF + Cl_2$
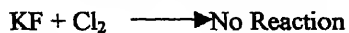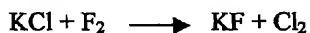
Fluorine shows only -1 oxidation state whereas other halogens also show $+1$, $+3$, $+5$ & $+7$ oxidation states. It is due to absence of d-orbital in F.

Strength of Oxyacids of Cl.

$$HClO < HClO_2 < HClO_3 < HClO_4$$
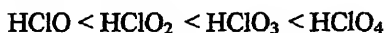
Due to increase the oxidation state of Cl from $+1$ to $+7$

Noble gas

Neel Bartlett Experiment (1962)

$$O_2 + Pt\ F_6 \longrightarrow O_2^+\{\ Pt + F_6\}^-$$
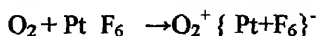
Since the I.P. of O_2 and Xe are comparable

i.e. Xe $= 1170$ Kjmol^{-1} $O_2 = 1166$ Kjmol^{-1}

$Xe + PtF_6 \rightarrow Xe^+[PtFe]^-$
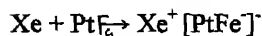
The compounds of Xe were discussed in detail Preparation,. Properties . and Structures have been discussed.

$\underset{2\ :\ 1}{Xe + F_2}\ \xrightarrow{673\ K}\ XeF_2$ During the preparation of these compounds the Ratio should be correct. If ratio is not correct then

$\underset{1:5}{Xe + F_2}\ \xrightarrow{673K}\ XeF_6$ desired compound will not be obtained.

$\underset{1:20}{Xe + F_2}\ \xrightarrow{673K}\ XeF_6$

XeF$_2$ is linear   F$-$Xe$-$F   Three lone pairs and two bond pairs
$120°C$

(sp^3 d hybridization)

XeF$_4$ is square planar   Two lone pairs and four bond pairs
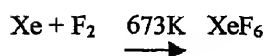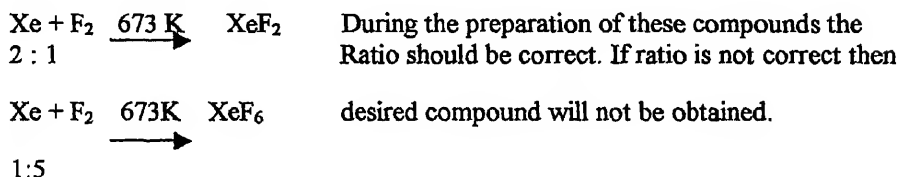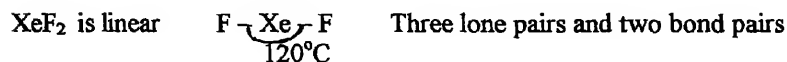
(sp^{3}d^2 hybridization)

XeF_6 is octahedral

$(sp^3d^3$ hybridization $)$
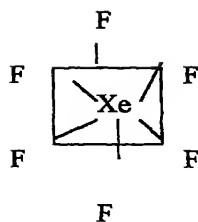
One lone pair and six bond pairs

TRANSITION ELEMENTS

Dr. Sulekh C. Agrawal

First of all a question arises why these elements are known transition elements ?

These elements are present between s-block i.e. highly electropositive and p block elements which are least electropositive or highly electronegative. The change (transition) from most electropositive to least electropositive takes place through these elements. Therefore these elements are known as transition elements.

However, the most appropriate definition of transition elements is:

Transition elements are those elements whose have partially filled d-orbitals either in atomic or in commonly occurring oxidation states.

Almost all the transition elements have partially filled d-orbital in atomic states. But the elements of group 11 i.e. Cu, Ag & Au have partially filled d-orbital in their common oxidation states such as Cu^{2+} Ag^{2+} & Au^{3+}

$$(3d^9), (4d^9), \quad (4d^8)$$
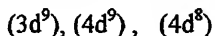
However, it may be noted that the above definition does not include elements of group 12 i.e. Zn, Cd and Hg. These elements do not have partially filled d-subshells in their atomic or in ionic form. But these elements may be treated along with transition elements because they are quite similar to other transition elements in some of their chemical properties.

Electronic Configuration:- They have general electronic configuration $(n-1)d^{1-10} \, ns^{0,1,2}$

It is quite interesting to note that after filling 3p of orbital, electron does not enter in 3d but eneter in 4s Why ?

This can be explained by n+l Rule.

The electron first enters into that orbital for which the value of n+l is less. The value of n+l for 3d is 5 and 4s is 4. Therefore, electron enter into 4s.

Further it is also interesting that when electron is removed, it is removed from 4s instead of 3d. It is due to low value of I.P for 4s electron as compared to 3d.

There are four transition series.

First (3d) transition series	SC to Zn
	21 30
Second (4d) transition series	Y to Cd
	39 48

Third (5d) transition series	La	Hf	to	Hg
	57	72		80

Fourth (6d) transition series	AC	Rf	to	uub
	89	104		112

Electronic Configuration of 3d transition series

Symbol	Atomic No.	Outer electronic configuration
SC	21	$3d^1 4s^2$
Ti	22	$3d^2 4s^2$
V	23	$3d^5 4s^2$
Cr	24	$3d^5 4s^1$
Mn	25	$3d^5 4s^2$
Fe	26	$3d^6 4s^2$
Co	27	$3d^7 4s^2$
Ni	28	$3d^8 4s^2$
Cu	29	$3d^{10} 4s^1$
Zn	30	$3d^{10} 4s^2$

The electronic configuration of Cr and Cu can be explained in terms of half filled and filled d-orbital which are more stable than that of partially filled.

However, there is no regular trends in the electronic configuration of other transition series. Two factor will work simultaneously

1. Electron – Electron repulsion

2. Electron – Nuclear attraction

General Physical properties

All the transition elements are metals. They are good conductor of heat and electricity. They are malleable and ductile. They show high m.p and B.P. due to strong intermetallic bonding. As the number of electron are available for bond formation m.p. & B.P. increase. They show high densities due to small size. They show higher heat of atomization. 4d and 5d block elements have a tendency to form M-M-bonds.

The atomic radii of the elements of a particular series decreases with increase in atomic number. But this decrease becomes small after midway due to screening effect of d-electrons. The atomic radii of 5d series elements are almost same to that of 4d series, due lanthanide contraction.

On the basis of I.P. and electrode potential the stability of oxidation states can be explained .

Characteristic properties:

(1)   Variable oxidation states:

Transition elements exhibit a large number of oxidation states. These different oxidation states are related to the electronic configuration of their atoms.

They show different oxidation states due to the participation of inner (n-1) electrons in addition to outer ns electrons because, the energies of the ns and (n-1) d-subshells are almost equal.

Element	Oxidation State
SC	+2, [+3]
Ti	+2 +3 [+4]
V	+2 +3 [+4] +5
Cr	(+1) +2 +3 (+4) (+5) + 6
Mn	[+2] +3, +4, (+5), +6, +7
Fe	+2 [+3] (+6)
Co	+2, +3
Ni	[+2] (+3) (+4)
Cu	+1, [+2]
Zn	[+2]

O.S in [   ] are most stable but (   ) are less stable

<u>Coloured ion:</u>____The most of the transition elements and their compounds are coloured. The colour is due to presence of unpaired electrons.

In case of transition elements, the electrons can be easily promoted from one energy level to another in the same d- subshell. The amount of energy required to excite some of the electrons to higher energy states within the same d-subshell corresponds to energy of certain colours of visible light.
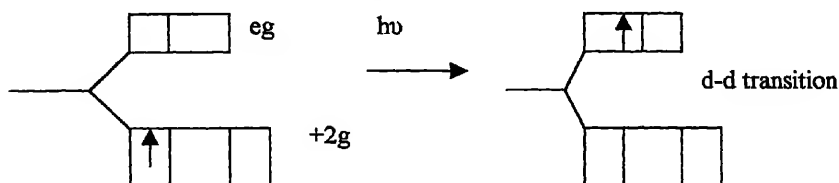
(In case of Octahedral complexes)

<u>Complex formation:</u> All the transition elements form complexes due to

(1)   Small size

(2)   Variable oxidation states

(3)   Vacant d-orbital to accept the pair of e^- from ligands.

<u>Magnetic properties</u>:

Due to presence of unpaired electrons all the transition elements are paramagnetic. The magnetic moment can be calculated.

$$\mu elp = \sqrt{n(n+2)} \quad B.M.$$

Where n = is the no. of unpaired e^-

For example Cu^{2+} ion has one unpaired e^- Therefore, its magnetic moment will be

$$\sqrt{1(1+2)} = \sqrt{3} \quad = 1.73 \ B.M.$$

<u>Catalytic Properties</u>::

Transition elements act as catalysts:

For example (i) Fe_2O_3, Haber's process of NH_3

(ii) V_2O_5, contact process of H_2SO_4

(iii)Ni, rainy vegetable oil in Ghee

(iv)MnO_2, for the decomposition of $KClO_3$

Explanation of Calalytic activities

(2)   Due to variable O.S.

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

It can be explained:

$SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$

$V_2O_4 + O_2 \rightarrow V_2O_5$
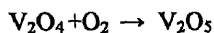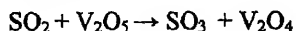
(i)   Due to formation of reaction intermediates. They lower the activation energy.

Alloy formation:

Due to almost same size they form alloys. They are hard and high M.P. solids.

Interstitial Compounds: With small elements such as H, B, C , N etc they form interstitial compounds. These are trapped in vacant spaces of transition metals and become rigid and hard.

f-BLOCK ELEMENTS

Dr. Sulekh C. Agrawal

The elements in which the last electron enters the f-orbital of their atoms are called f-block elements. These element are also called inner transition elements. They consist of two series of elements placed at the bottom of the periodic table. These series are formed due to filling of 4f and 5 f orbitals.

<u>4f or Lanthanides:-</u>

The series involving the filling of 4f-orbitals following lanthanum is called lanthanides. There are 14 elements in this series starting from Ce(58) to Lu (71). These elements are found as rare in earth and therefore, these elements have also been called rare earth elements.

General Characteristics of Lanthanides:

Electronic configuration: The Lanthanides involve the gradual filling of 4f orbitals. It may be noted that the energy of 5d and next inner shell f-orbitals are nearly similar and therefore, the order of filling the 4f orbitals in the atoms shows quite irregularities.

The electronic configuration of Lanthanides is given below. The general electronic configuration is $(n-2) f^{2-14} (n-1)d^{0,1} ns^2$.

Element	Atomic No.	Outer electronic configuration
Ca	58	$4f^2 5d^0 6S^2$
Pr	59	$4f^3 5d^0 6S^2$
Nd	60	$4f^4 5d^0 6S^2$
Pm	61	$4f^5 5d^0 6S^2$
Sm	62	$4f^6 5d^0 6S^2$
Eu	63	$4f^7 5d^0 6S^2$
Gd	64	$4f^7 5d^1 6S^2$
T_6	65	$4f^9 5d^0 6S^2$
Dy	66	$4f^{10} 5d^0 6S^2$

Ho	67	$4f^{11}5d^{0}6S^{2}$
En	68	$4f^{12}5d^{0}6S^{2}$
Tm	69	$4f^{13}5d^{0}6S^{2}$
Yb	70	$4f^{14}5d^{0}6S^{2}$
Lu	71	$4f^{15}5d^{1}6S^{2}$

The actinides involve the filling of 5f Actinium has electronic configuration $6d^{1}\,7s^{2}$. From thorium (Z=90) onwards 5f-orbitals get progressively filled. Because of almost equal energy of 5f and 6d subshell there are some irregularities regarding the filling of 5f and 6d subshells. The electronic configuration is given below.

Element Symbol	Z Atomic No.	Outer electronic configuration
Th	90	$5f^{1}6d^{1}7S^{2}$
Pa	91	$5f^{2}6d^{1}7S^{2}$
U	92	$5f^{3}6d^{1}7S^{2}$
Np	93	$5f^{4}6d^{0}7S^{2}$
Pu	94	$5f^{6}6d^{0}7S^{2}$
Am	95	$5f^{7}6d^{0}7S^{2}$
Cm	96	$5f^{7}6d^{1}7S^{2}$
Bk	97	$5f^{9}6d^{0}7S^{2}$
Cf	98	$5f^{10}6d^{0}7S^{2}$
Es	99	$5f^{11}6d^{0}7S^{2}$
Fm	100	$5f^{12}6d^{0}7S^{2}$
Md	101	$5f^{13}6d^{0}7S^{2}$
No	102	$5f^{14}6d^{0}7S^{2}$
Lr	103	$5f^{14}6d^{0}7S^{2}$

Oxidation State

The characteristic oxidation state of 4f- elements is +3. However, some elements also show +4 and +2 Oxidation states. In most of the cases +4 and +2 are due either the 4f vacant, Half filled or fully filled.

$$Ce^{4+} = 4f^{\circ} \qquad Tb^{3+} = 4f^7$$

$$Eu^{2+} = 4f^7 \qquad Yb^{2+} = 4f^{14}$$

Some other elements show +4 and +2 which do not have electronic configuration $4f^{\circ}$ $4f^1$ or $4f^{14}$ but those O.S. are not stable.

Actinides show variable oxidation state, which is due to the energy of 5f and 6d orbital is almost same. They show +2, +3, +4, +5, +6 oxidation states.

Lanthanides are soft, malleable and ductile with low tensile strength.

Colour:- The colour is due to f-f transition for the same oxidation state the colour of f^n will be same as of (14-n)f. The colour of these metal ion is not affected by external environment.

Magnetic Properties:

Paramagnetic. The magnetic moment values for lanthanides are higher as compared to d-block elements.

Atomic & ionic Radii

The atomic radii of lanthanides decrease from La to Lu except Eu & Yb. These two elements involve only two electrons in bonding and others three. However the ionic radii decrease for particular O.S. from La^{3+} to Lu^{3+}. The decrease in ionic radii is due to imperfect shielding of valence electron by 4f or 5f electrons.

The regular decrease in radii is known as Lanthanide or Actinides contraction.

Consequences of Lanthanide contraction:

(1)Acid character increases

(2)Due to almost same size, it is difficult to separate them.

(3)They also effect the chemistry of post lanthanide elements.

Comparison of Lanthanide & Actinides

Oxidation state	Lanthanide shows +3 oxidation state with few exception	Actinides show variable oxidation state
Complex formation	Less	They form complexes
Basic character	Less	more
Oxo-ions	Not formed	formed $(UO_2{}^{2+})$
Radioactive	Only Pm is radioactive	All elements are radioactive

ORGANOMETALIC COMPOUNDS

Dr. Sulekh C. Agrawal

This type of compounds are also generally studied along with complexes. The main difference between complexes and organometallic compounds in the complexes the bonding is between metal and any other donor atom such as O.N.F. etc. whereas organometallic bonding, between M and carbon.

These can be defined as

The organometallic compounds are those compounds which contain one or more metal-carbon bonds. For example Ti $(OC_2H_5)_4$ is not an organometallic compounds because there is no metal-carbon bond. But Ti $(OC_2H_8)_3$ is an organometallic compound because it has one Ti-C bond.

Classification of Organometallic compounds.

Broadly the organometallic compounds have been divide into two categories.

1   σ -bonded (Metal-carbon covalent σ –bond)

For example Zn $(CH_3)_2$, RMgx, $Sn(CH_3)_4$ $B(CH_3)_3$, Sn $(C_2H_5)_4$, $(CH_3)_3$ Al

2.   π- bonded. No σ -bonding

K $[PtCl_3 (C_2H_4)]$, $Fe(C_5H_5)_2$, Cr $(C_6H_6)_2$

Preparation

σ - bonded only

$Mg+C_2H_5Br \longrightarrow C_2H_5Mg Br$

$2C_2H_5 Br + Zn \longrightarrow (C_2H_5)_2 Zn + Zn Br_2$

λ- bonded

$H_2C = CH_2 +K_2 P+Cl_4 \longrightarrow K [P+Cl_3 C_2H_4] + KCl$

$2C_5H_5MgBr + FeCl_2 \longrightarrow [(C5H_5)Fe] + 2Mg Br Cl$

$2C_6H_6+ Cr (vapours) \longrightarrow (C_6H_6)_2 Cr$
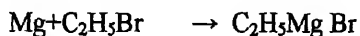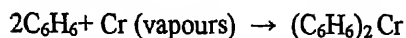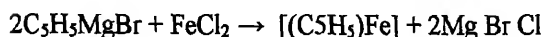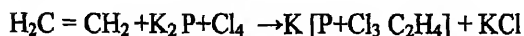
Structure
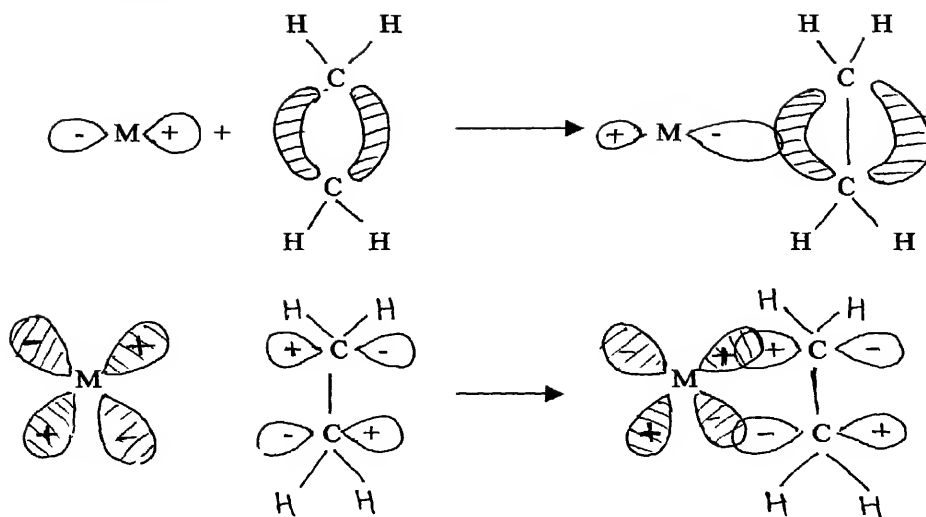
π - back bonding

Applications:

(1)   Wilkinson Catalyst

(2)   Ziglar Natta Catalyst

(3)   Pb(C₂H₅)₄ Anti knocking agent

(4)   Organometallic compounds are used in organic synthesis

(5)   C₂H₅ HgCl is used as fungicide

An Introduction to Polymers

-by Dr.R.Ravichandran
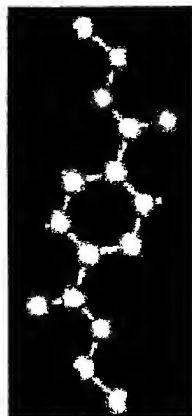
What Are Polymers?

Polymers are a very important class of materials. Polymers occur naturally in the form of proteins, cellulose(plants), starch(food) and natural rubber. Engineering polymers, however, are usually synthetic polymers. The field of synthetic polymers or plastics is currently one of the fastest growing materials industries. The interest in engineering polymers is driven by their manufacturability, recyclability, mechanical properties, and lower cost as compared to many alloys and ceramics. Also the macromolecular structure of synthetic polymers provides good biocompatibility and allows them to perform many biomimetic tasks that cannot be performed by other synthetic materials, which include drug delivery, use as grafts for arteries and veins and use in artificial tendons, ligaments and joints. A polymer is a material whose molecules contain a very large number of atoms linked by covalent bonds, which makes polymers macromolecules. Polymers consist mainly of identical or similar units joined together. The unit forming the repetitive pattern is called a "mer" or "monomer". Usually the biggest differences in polymer properties result from how the atoms and chains are linked together in space. Polymers that have a 1-D structure will have different properties than those that have either a 2-D or 3-D structue.

Polymer Structures

One-dimensional Polymers

One dimensional polymers are most common. They can occur whenever 2 reacting chains join to make a chain. If the long-chains pack regularly, side-by-side, they tend to form crystalline polymers. If the long chain molecules are irregularly tangled, the polymer is amorphous since there is no long range order. Sometimes this type of polymer is called glassy.

Two-dimensional Polymers

Two dimensional polymers are rare, the best example of one would be graphite. It is the structure of graphite which provides its great lubricating capability. The condition to form this planar structure is to have 3 or more active groups all directed in the same plane and capable of forming a planar network. This structure offers low shear strength and good lubricating properties.

Three-dimensional Polymers

Crystalline Diamond is an example of the 3-dimensional crystalline polymer in which carbon is linked to four corners of the tetrahedra and these are packed with long range order in space to form a lattice. Diamond has properties which are much more like ceramics than polymers in terms of mechanical behavior (high melting point, modulus, hardness, strength, and fracture behavior) because of this.

Polymer Classification Table

Form of Network		Form of Molecule		
		One Dimensional Linear	Two Dimensional Sheet	Three Dimensional Bulk
amorphous irregular	flexible chain	*rubbers* (natural,synthetic)		
	rigid chain	*glassy plastics* eg polystyrene	*thermoset plastics* eg polyester	
crystalline regular	partial unoriented	*tough plastics* eg nylon		
	partial oriented	*fibers and films* (natural,man-made)	eg carbon fibre	
	perfect	*single cyrstals* eg polyethylene	eg graphite	eg diamond

Classification of Polymers
Thermoplastic Polymers

These are linear, one-dimensional polymers which have strong intramolecular covalent bonds and weak intermolecular van Der Waals bonds. At elevated temperature, it is easy to "melt" these bonds and have molecular chains readily slide past one another. These polymers are capable of flow at elevated temperatures, can be remolded into different forms, and in general, are dissolvable. A thermoplastic, under the application of appropriate heat, can be melted into a "liquid" state.

Thermosetting Polymers

These are three-dimensional amorphous polymers which are highly crosslinked (strong, covalent intermolecular bonds) networks with no long-range order. Thermosetting polymers are those resins which are "set" or "polymerized" through a chemical reaction resulting in crosslinking of the structure into one large 3-

dimensional molecular network. Once the chemical reaction or polymerization is complete, the polymer becomes a hard, infusible, insoluble material which cannot be softened, melted or molded non-destructively. A good example of a thermosetting plastic is a two-part epoxy systems in which a resin and hardener (both in a viscous state) are mixed and within several minutes, the polymerization is complete resulting in a hard epoxy plastic.

Rubbers and Elastomers
In general, a rubber material is one which can be stretched to at least twice its original length and rapidly contract to its original length. Rubber must be a high polymer (polymers with very long chains) as rubber elasticity, from a molecular standpoint, is due to the coiling and uncoiling of very long chains. To have "rubber-elastic properties" a rubber materials' use temperature must be above its glass transition temperature and it must be amorphous in its unstretched state since crystallinity hinders coiling and uncoiling. Rubbers are lightly crosslinked in order to prevent chains from slipping past one another under stress without complete recovery. "Natural rubber" is a thermoplastic, and in its natural form it becomes "soft" and sticky" on hot days (not a good property for an automobile tire). In fact, until Mr. Goodyear discovered a curing reaction with sulfur in 1839, rubbers were not crosslinked and did not have unique mechanical, rubber-elastic properties.

Fibers
Many of the polymers used for synthetic fibers are identical to those used in plastics but the two industries developed separately and employ different testing methods and terminology. A fiber is often defined as having an aspect ratio (length/diameter) of at least 100. Synthetic fibers are spun into continuous filaments, or chopped in shorter staple which are then twisted into thread before weaving. The thickness of the fiber is expressed in terms of denier which is the weight in grams of a 9000-m length of fiber. Stresses and strength of fibers are reported in terms of tenacity in units of grams/denier. In melt spinning, polymer pellets are gravity fed into an extruder and subjected to shear loading at elevated temperatures. The softened polymer is delivered to the spinneret which has up to 1000 shaped holes for fiber formation. A molten stream of polymer is forced by pressure through shaped holes and stretched into a solid state. Then the polymer is streched to have molecular alignment along the axial direction and crystallized in a preferred direction so that no spherulites form. Synthetic fibers include Kevlar, carbon, PE, PTFE, and nylon while natural fibers include silk, cotton, wool and wood pulp.

Liquid Crystals
The structure of liquid crystals such as Spectra 1000 is unique. It is a near-ideal in structure with most of its molecules virtually stretched out. While this is not useful for textiles, it is excellent for composite reinforcement. Continuous crystals are readily attained in liquid crystalline polymers, as the molecules are already aligned

in parallel positions in the melt whereas the continuous morphology of PE would require elaborate processing to avoid chain entanglement and chain folding.

Polymer Synthesis
Step Growth
In step growth polymerization or condensation polymerization, chains of any lenght x and y combine to form long chains. x-mer + y-mer --> (x + y)-mer

Synthetic step growth polymers have been around since the late 1920s. The term condensation polymerization comes from this time period, because the early reaction yielded water. More recently it has been found that several other polymer reaction will condense out products such as HCl or will condense out no products. Step growth polymerization is used to yield branched as well as networked polymers. The true initator of a network structure lines in a multifunctional monomer. As the length and frequency of branches on the polymer chain increases so does the probability that the branches will reach from chain to chain. When all the chains are connected together the entire polymer mass becomes one giant molecule. Consider a bowling ball, it has a molecular weight on the order of 10^{27} g/mol, and it is one giant molecule. Crosslinked or network polymers form in one of two ways:

1. Starting with tri functional (or higher) monomers
2. Chemically creating crosslinks from previous linear polymers

Chain Growth
Chain growth polymerization involves an active chain site which reacts wiht an unsatureated (or heterocyclic) monomer such that the active site is recovered at the chain end. Vinyl polymers were probably the first to be synthesized in this manner when in 1839 Simon reported the conversion of styrene to some gealtinous mass. In general, high molecular weight species are made by the successive addtion of new monomers to the chain end. There are several different techniques of synthesis depending on the active site. These are:

Active Site	Synthesis Technique
Free Radicals	Free Radical Polymerization
Carbanions	Anionic Polymerization
Carbenium Ions	Cationic Polymerization
Coordination Bonds with Transition Metals	Ziegler-Natta Polymerization

Transitions in Polymers
Amorphous polymers exhibit two distinctly different types of mechanical behavior. Some, like polymethyl methacrylate and polystyrene are hard, rigid, glassy plastics at room temperature while others like polybutadiene and polyethyl acrylate are soft, flexible, rubbery materials at room temperature. There is a temperature, or range of

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temperatures, below which an amorphous polymer is in a glassy state and above which it is rubbery. This temperature is called the glass transition temperature, Tg, and it characterizes the amorphous phase. It is especially useful since all polymers are amorphous to some degree, they all have a Tg.

Molecular Motions in Amorphous Polymers
The molecular motions occuring inside an amorphous polymer influence the glass transition temperature. The important motions are:
1. Translation motion of entire molecules (permits flow)
2. Cooperative wriggling and jumping of segments of molecules (permits flexing and uncoiling leading to elasticity)
3. Motions of a few atoms along the main chain or side groups on the main chain
4. Vibrations of atoms about equilibrium position

The glass transition temperature is the temperature at which there is only enough energy for motions (3) and (4) to occur. Below the glass transition temperature processes (1) and (2) are frozen out. This makes the the material is "glassy" below Tg and "rubbery" above Tg.

Factors Influencing Glass Transition Temperature
In general the glass transition temperature depends on five other factors which are:
1. Free volume of the polymer vf, which is the volume of the polymer mass not actually occupied by the molecules themselves. The higher vf is the more room the molecules have to move around and the lower Tg is. For all polymers the ratio of the free volume vs the total volume (vf/v) is about 0.025 at Tg.
2. The attractive forces between the molecules. The more strongly the molecules are bound together , the more thermal energy must be applied to produce motion.
3. The internal mobility of the chains, or their freedom to rotate about the bonds.
4. The stiffness of the chains. Stiff chains cannot easily coil and fold, causing Tg to be higher for polymers with stiff chains. Polymers with parallel bonds in the backbone, like polyimides, and polymers with highly aromatic backbones have extremely stiff chains and thus high Tg's.
5. The chain length. The glass transition temperature varies according to the relation:
   Tg = Tinf - C/x
   where C is a polymer specific constant, Tinf is the asymptotic value of the glass transition temperature for a chain of length infinity and x is the length of the chain. This relationship shows that shorter chains can move easier than longer chains. For most commercial polymers Tg ~ Tinf, since x is quite long.

Determination of the Glass Transition Temperature
The most common method used to determine Tg is to observe the variation of a thermodynamic property with T. Tg determined in this manner will vary somewhat depending on the rate of cooling or heating, which reflects the fact that long entangled polymer chains cannot repsond instantaneously to changes in temperature. At the glass transition temperature a thermodynamic property will exhibit a discontinuity with termperature, thus it is classified as a second order thermodynamic transition.

Interesting Tidbits
- One of the first developments of plastics was as a replacement to ivory billard balls, due to the dwindling supply of ivory. As far back as 1866, elephants were being slaughtered at an alarming rate to keep up with the demand for ivory billiard balls, billards having become America's favorite pastime. John Wesly Hyatt, invented the replacement, one of the first plastics, called celluloid, which was used in movies for a short time.
- An important plastics inventor was Charles Macintosh, who developed a plastic coated waterproof fabric in the mid 19th century and gaves is name to the coat. In Britian, people still refer to thier raincoats as "Macs".
- The inventor of the first synthetic plastic, Bakelite, was Leo Bakeland. Time magazine called him "The King of Plastics" and put him on the cover of its September 22, 1924 issue. It dubbed Bakelite`"The material with a thousand uses".
- In the 1940's a vinyl based material commonly known as Saran Wrap started as a furniture protector. During World War II defense contractors found more important uses for the plastic. Saran film "sprayed" on plane being shipped overseas protected them from the salty sea spray, which meant that the process of disassembling, greasing at the point of origin and then cleaning and reassembling at the destination were avoided. After the war there was an oversupply of the film and resulted in it being marketed as the self cling food wrap we find in kitchens everywhere.
- Also during the 1940's started the craze for nylon stockings, which were rumored to be so strong that only an acetylene torch could but a run in them. Manufactures claimed that the nylon stockings were as "strong as steel" and lead many women to believe that the hose were impervious to razor blades and nail files. Nylons were so popular that women stampeded to get even one pair.
- One of the most well known plastics of today, GORE-TEX, which is sued to make extremely warm jackets and shoes, is used extensively in vascular grafts and patches for heart defects and hernias.

SEPARATION OF PIGMENTS PRESENT IN SPINACH LEAVES BY PAPER CROMATOGRAPHY

Dr. Rashmi Sharma

Paper chromatography is an important and useful class of partition chromatography. In this technique the stationary phase is considered to be made up of water molecules supported on whatman filter paper No.1. The mobile phase consists of either one solvent or mixture of different solvents. Separation of the mixture into pure substances takes place by partitioning of different substances between the two liquid phases. Different components of the mixture travel with different speeds but it is always less than the speed of the mobile phase (solvent). The ratio of the distance travelled by the solvent is called Rf value.

Rf = Distance traveled by the solute

Distance traveled by the solvent front

The Rf values depend on the nature of the substance, nature of solvent, quality of paper, temperature.

The spinach leaves contain, chlorophyll a and b Xanthophyll, carotene. The Rf values of chlorophyll b and a, Xanthophyll and carotene for petroleum ether and acetone solvent mixture are 0.45, 0.65, 0.71 and 0.95 respectively.

If the concentrated extract of leaves is applied on the paper and the chromatogram is developed using a mixture of solvents (petroleum ether: acetane (5:1), the pigments travel with different speeds with the developing solvent depending upon their Rf values and thus separation takes place. The separated pigments can be identified on the basis of their different colours.

Apparatus: A boiling tube having a cork, drawing pins, whatman filter paper No.1, A fine capillary tube, scale, pencil.

Chemicals required: Spinach leaves, acetone petroleum ether, pestle, mortar,

Procedure: With the help of a scissor cut a strip of whatman paper of length and width suitable for boiling tube. Place the strip flat on the table and with the help of a pencil and scale draw a line at a distance of about 3 cm from one end parallel to the width. Grind fresh leaves in a mortar with a pestle. Extract the juice by adding acetone and then filter With the help of a fine capillary, put a drop of the juice on the line's center by gently touching the end of the capillary. Dry it and again apply the juice at exactly same place (Take care that diameter of the spot should not 0.5cm) repeat it 5-10 tomes. Fold about 1-2 cm of the paper from the end other than the one containing the spot and fix it on the inner side of the cork with a drawing pin so that cork is fitted into the mouth of the boiling tube, the paper strip hangs freely (not touching the wall of the boiling tube) . Take developing solvent (petroleum ether: acetone 5: 1) into the boiling tube to have its height 1-2 from the bottom. Now dip the filter paper strip to nearly 1 cm in the solvent in such a way that the spot remains above the level (near 1 cm) of solvent. Leave apparatus undisturbed for 15- 30 minutes till solvent front travels nearly 10-15 cm from the point of application. (should be stopped before it reaches the other end of the paper, so that other end is left at about 1-2 cm from the solvent front). Take out the strip and mark with pencil the level to which the solvent has reached. Let the paper dry. We will see a different spots of the pigments. Mark them also. Measure the distances of the spots and that of the solvent front from the initial point and find out Rf values.

Observations and Calculations

1.Developing solvent (petroleum ether: acetone 5: 1)

2.Room temperature = $^{\circ}$c

3.Distance traveled by the solvent frame = cm

Name of the Pigment	Colour of the spot	Distance traveled by the spot	Rf Value
Chlorophyll-b	green		
Chlorophyll-a	bluish green		
Xanthophyll	yellow-brown		
Carotenes	yellow-red		
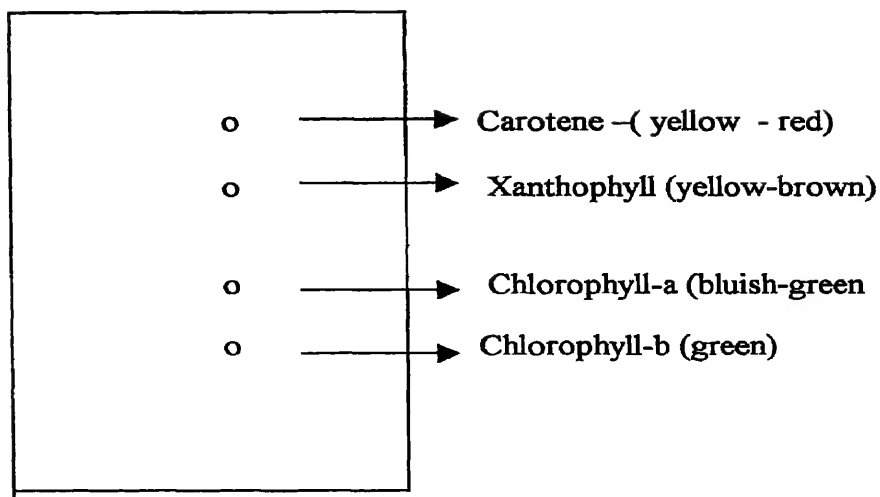
Fig: Spots on the paper after development

Result: The Rf values of the pigments are as below

Chlorophyll-b   ---------------

Chlorophyll -a   ---------------

Xanthophyll   -------------

Carotine   ---------------

ENVIRONMENTAL CHEMISTRY

Dr. R.S. Sindhu

Environmental chemistry deals with the study of the chemical species existing in the various segments of the environment, their sources, pathways, reactions and their consequences on the activities of human beings and other life-forms.

One of the most important domains of study of environmental chemistry is environmental pollution which is caused by solid, liquids or gases when they are in such concentration as may be or tend to be injurious to part or parts of environment.

In general environmental pollution is classified on the basis of segment of the environment being polluted and this way mainly two types of pollutions are of main concern. They are; air pollution and water pollution.

Air Pollution: According to WHO, air pollution may be defined as:

"Substances put into air by the activity of mankind into concentration sufficient to cause harmful effect to his health, vegetables, property or to interfere with the enjoyment of his property".

The air pollutants may be gaseous or particulate. The gaseous pollutants are oxides of sulphur (SO_2, SO_3), oxides of nitrogen (mainly NO_2 produced in air by oxidation of NO), oxides of carbon (CO, CO_2). The particulate pollutants comprise of finely divided solids or liquids and often exist in colloidal state as aerosols, e.g. smoke, fumes, dust mist, fog, smog and sprays.

<u>Effect of air pollution on the environment</u>

(1) Effect on materials: The materials that may be affected by air pollutants include metals, building materials, rubbers, paper, textiles, leather, dyes, glass enamels and

surface coatings. The damages caused can be corrosion, abrasion, deposition, direct chemical attack and indirect chemical attack.

(ii) Effect on Vegetation: Oxides of sulphur, nitrogen, HF, smog, oxidants, like ozone, chlorine, herbicide and weedicide sprays exert toxic effects on vegetation. The damages caused can be visual inquiry such as chlorotic marking, banding, silvering or bronzing of the underside of the leaf. Retardation of plant growth also may occur.

(iii) Effect on animals – The air-borne contaminants like arsenic, lead and fluorides by entering into vegetation act as poison for the animals.

(iv) Reduction in visibility in atmosphere : The air when polluted by heavy smoke fog or dust storms becomes dark in colour. Its colourlessness decreases and thus causes decrease in visibility.

(v) Effect on human being: Air pollution affects the health of human being. Sulphur dioxide can cause acute irritation to the membrane of the eyes resulting in tears and redness, cough, shortness of breath. NO_2 is extremely toxic to living tissues. CO is poisonous because it binds to haemoglobin much more strongly than oxygen. Depending upon the concentration, CO in the blood can cause mental impairment, obstructed respiration, dizziness and even death. CO_2 causes mild narcotic effects, stimulation of the respiratory center and leads to asphyxiation.

Air pollution causes two important phenomena known as "green house effect" and "acid rain". Both were discussed in the programme in length. Due to increase in concentration of CO_2, chlorofloro carbons (CFCs), methane etc. green house effect occurs which levels to global warming. Acid rain is defined as the rain in which water's pH is lesser than 5.6. This is caused mainly due to oxides of sulphur and nitrogen. These gases form acids in the water of rain.

Water Pollution

Water pollution can be defined; " condition caused by addition to water of an excess of material that is harmful to humans, animals or desirable aquatic life or otherwise causes harmful significant departures from the normal activities of various living communities in or near bodies of water, is known as water pollution". In reality the term water pollution refers to any type of aquatic contamination between two extremes: (1) a highly enriched, over productive boitic community, such as a river or lake with nutrients from sewage or fertilizer (cultural eutrophication) or (2) body of water poisoned by toxic chemicals which eliminate living organisms or even exclude all forms of life.

Water pollution can be classified into the following types.

1.   Sewage and other oxygen demanding   wastes: These have been largely carboneous organic materials that can get oxidized by micro organisms to CO_2 and $H_2 O$. Sewage and other oxygen demanding wastes have been classified as water pollutants because their degradation leads to oxygen depletion which affects fish and other aquatic life.

2.   Infectious agents: Waste water related from municipalities, sanitoria, tanning and slaughter house and boats may be a source of bacteria or other organisms which are capable of producing disease in men and animals.

3.   Plant nutrients: Plant nutrients like N, P are able to stimulate the growth of aquatic plants which interfere with water BOD. The enrichment of waters by nutrients is termed as eutrophication. Over periods of many millennia, the aging of lakes and slow moving waters through eutrophication gives rise to their conversion into swamps and marshes. Man-made eutrophication hastens this process.

4.   Exotic organic chemicals: The exotic organic chemicals include surfactants in detergents, pesticides, various industrial products, and the decomposition products of other organic compounds. Many of these chemicals are toxic to aquatic organisms.

5.   Inorganic pollutants: In a number of chemical processes, waste inorganic materials enter water. Important examples are mercury as CH_3 Mg^+, bromine, iodine, FeS_2, Cd, Pb. Cadminum and mercury can cause kidney damage and lead poisoning can cause damage to the liver, kidney, brain and central nervous system.

6   Sediments: Sediments are soil and mineral particles which are washed from the land by storms and flood waters from croplands, unprotected forest soils, strip mines, roads and bulldozed urban areas. Sediments are able to reduce the amount of sunlight available to green aquatic plants, plug water filters and blanket fish nests, spawn and food supplies, thus, reducing the fish and shellfish populations.

7.   Radioactive substances. Harmful radiation may result in water from the wastes of uranium and thorium mining and refining from nuclear power plants and from industrial, medical and scientific utilization of radioactive materials.

Effects of Water Pollution: Water pollution adversely affects human health, aquatic life. Many water pollutants are toxic to the plants, animals and human being. Even the recreation areas are also lost due to water pollution.

PROJECT WORK

Dr. Rashmi Sharma

Learning of science in schools develops the spirit of enquiry, creativity, objectivity and aesthetic sensibility. All these can be achieved if in the learning of science main emphasis is given on the processes. The best way of getting training in science processes is to undertake a project. Chemistry discipline is central to all natural sciences. Therefore, if the project is undertaken related to chemistry problem, one is trained in all science processes. The project work usually implies the separate following of individual problems by student or students over a period of few days or a few weeks and such problem may include several sub-problems. It may involve a variety of activities and mostly results in physical outcome – product, written report or display.

The various steps involved in a project are:

1. To select a problem

2. To collect all possible literature concerning the problem.

3. To set up experiments to study the problem.

4. To record the observations

5. To arrange the observations in a systematic way.

6. To interpret the results

7. To draw conclusions and make generalizations

8. To write the project

The following are the characteristics of a good project.

1. It should be purposeful. Every project should be applicable to real life situations

2. The students should develop scientific temper

3. The students should work independently. The teacher's work should be that of facilitator only

4. It should be economical

5. The project should be neither too simple and easy nor too long and difficult.

6. It should be feasible within the facilities available.

The format of writing a project

When the project work has been completed, the student has to write the project in typed or printed form. The following format of writing the project is suggested.

The first page should consist of the following informations in the format as given below:

Title of the project

Submitted by

Name of the Worker

Class

Name of School

Session

Second page should contain the certificate from the teacher about the authenticity of the work. Format of the certificate can be as below.

This is to certify that the project work entitled "…………………………….." has been done by Mr……………………………….class………. ………….. under my supervision.

Dated: Signature of the Teacher

                                              (Name of the Teacher)

The third page should have heading "Acknowledgement". Under this title the students should express his thanks for academic support and infrastructure facilities provided by the teachers school and other agencies. In the last his signature with name should be given. The date should be written on left hand side.

The fourth and subsequent pages should contain the following titles of the work on separate pages.

1.   Introduction,   2.   Aims and objectives (3)   Experimental

(4)   Results and Discussion   (5) Summary   (6) References.

The following investigatory project can be taken as an example.

Preparation of Map of Hardness of Water of Bhopal City.

For carrying out this project, the water samples from different directions should be collected and then by EDTA titration the hardness of each sample should be found in ppm of calcium carbonate. Then, on the map of Bhopal these data should be written Thus a map of hardness of water is prepared.

Appendix I

Time Table

23rd August, 2004

9.30 am.. – 10.30 am.	-	Registration and Inauguration
10.30 am – 11.00 am	-	Tea Break
11.00 am - 12.00 noon	-	Organic Chemistry

Some basic principles – I
Dr. V.P. Gupta

12.00 noon – 1.00 pm	-	Solid state – I

Prof. G.T. Bhandage

1.00 pm - 2.00 pm	-	Lunch
2.00 pm - 3.00 pm	-	Representative Elements – I

Dr. Sulekh Chandra Agarwal

3.00 pm - 3.30 pm	-	Tea Break
3.30 pm - 4.30 pm	-	Electrochemistry - I

Dr. (Mrs) Charanjeet Kaur

4.30 pm - 5.30 pm	-	Qualitative Analysis

Dr (Ms) Rashmi Sharma

24th August, 2004

9.30 am - 10.30 am	-	Organic Chemistry – Some basic principles- II

Dr. V.P. Gupta

10.30 am - 11.00 am	-	Tea Break
11.00 am - 12.00 noon	-	Representative Elements – II

Dr. Sulekh Chandra Agarwal

12.00 noon - 1.00 pm	-	Polymers

Dr. R. Ravichandran

1.00 pm - 2.00 pm	-	Lunch

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2.00 pm	-	3.00 pm	-	Stereochemistry - I Dr. V.P. Gupta
3.00 pm	-	3.30 pm	-	Tea Break
3.30 pm	-	4.30 pm	-	Electrochemistry – II Dr.(Mrs) Charanjeet Kaur
4.30 pm	-	5.30pm	-	Instructional Materials – I Dr.(Ms) Rashmi Sharma

25th August, 2004

9.30 am	-	10.30 am	-	Transition Elements Dr. Sulekh Chandra Agrawal
10.30 am	-	11.00 am	-	Tea Break
11.00 am	-	12 noon	-	Stereochemistry – II Dr. V.P. Gupta
12.00 noon	-	1.00 pm	-	Separation of pigments of plant leaves by paper chromatography Dr.(Ms) Rashmi Sharma
1.00 pm	-	2.00 pm	-	Lunch
2.00 pm	-	3.00 pm	-	Aromaticity Dr. V.P. Gupta
3.00 pm	-	3.30 pm	-	Tea Break
3.30 pm	-	4 30 pm	-	Chemical Kinetics - I Dr.(Mrs) Charanjeet Kaur
4.30 pm	-	5.30 pm	-	Solid State - II Prof. G T. Bhandage

26th August, 2004

9.30 am	-	10.30 pm	-	Coordination Compounds - I Dr. R.S. Sindhu
10.30 am	-	11.00 am	-	Tea Break
11.00 am	-	12.00 noon	-	Thermodynamics Prof. G.T. Bhandage
12.00 noon	-	1.00 pm	-	f – Block elements Dr. Sulekh Chandra Agarwal

1.00 pm	-	2.00pm	-	Lunch
2.00 pm	-	3.00 pm	-	Instructional Materials - II
				Dr. (Ms) Rashmi Sharma
3.00 pm	-	3.30 pm	-	Tea Break
3.30 pm	-	4.30 pm	-	Chemical Kinetics – II
				Dr. (Mrs) Charanjeet Kaur
4.30 pm	-	5.30 pm	-	Chemistry in Everyday Life
				Dr. R. Ravichandran

27th August, 2004

9.30 am	-	10.30 am	-	Coordination Compounds – II
				Dr. R.S. Sindhu
10.30 am	-	11.00am	-	Tea Break
11.00am	-	12.00 noon	-	Projects
				Dr.(Ms) Rashmi Sharma
12.00 noon	-	1.00 pm	-	Organometallic Compounds
				Dr. Sulekh Chandra Agarwal
1.00 pm	-	2.00 pm	-	Lunch Break
2.00 pm	-	3.00 pm	-	Nuclear chemistry
				Dr.(Mrs) Charanjeet Kaur
3.00 pm	-	4.00 pm	-	Environmental Chemistry
				Dr. R.S. Sindhu
4.00 pm	-	5.30 pm	-	Valedictory function

Appendix II

List of Resource Persons

1.	Dr. V.P. Gupta	RIE, Aimer
2.	Dr.(Ms) Rashmi Sharma	Army Centre of Education, Pachmarhi
3.	Dr.(Mrs) Charanjit Kaur	Sri. Satya Said College, BHEL, Bhopal
4.	Dr. Sulekh Chandra	Zakir Hussain College, J.L.N.Marg, New Delhi
5.	Prof. G.T. Bhandage	RIE, Bhopal
6.	Dr. R.S. Sindhu	RIE, Bhopal
7.	Dr. R. Ravichandran	RIE, Bhopal

Appendix III
List of Participants

1. Mr. A. Nagabhushana Rao	Govt. Model Hr. Sec. School , Dantewada
2. Mrs. Arti Tiwari	Govt. Hr. Sec. School, Gourella Dist. Bilaspur
3. Mr. Narendra Kumar Tiwari	Govt. Girls Hr. Sec. Pendra, Dist. Bilaspur
4. Mrs. Rekha Yadav	Govt. Hr.. Sec. School, Haldibadi, Chirimiri Dist. Korea
5. Mrs. Anita Singh	Govt. Hr. Sec.. School, Lafa, Korba
6. Mrs. Preeti Shrivastava	Govt. Girls Hr. Sec. School, Marwahi, Dist. Bilaspur
7. Mr. A.P. Singh	Govt. Boys Hr. Sec. School, Ramanuj Ganj, Dist. Sarguja
8. Mr. S.P. Nishad	Govt. Hr. Sec. School, Karonji Dist. Surguja
9. Mrs. Rachana Shrivastava	Govt. Girls Hr. Sec. School, Bishrampur, Dist. Surguja
10. Mrs. Padma Singh	Govt. Boys Hr. Sec. School, Marwahi, Pendra
11. Mr. Hemraj Vishwakarma	Govt. Girls Hr. Sec. School, Marwahi, Bilaspur
12. Mr. V.P. Mishra	Govt. Girls Hr. Sec. School, Bada Bazar, Chirimiri Dist. Korea
13. Mrs. Sheejan Johnson	Govt. Boys Hr. Sec. School, Dondi, Dist. Durg
14. Mr. Basu Shankar Raha	Govt. Girls Hr. Sec. School, Dharamjaigarh, Raigarh
15. Mr. Sanjay Kumar Agrawal	Govt. Hr. Sec. School, Bhailaibazar, Korba
16. Mrs. A. Banerjee	Govt. Tribal Hr. Sec. School, Korba
(joined on 24.8.2004)	
17. Mr. Dilip Kumar Patel (joined on 24.8.2004)	Govt. Hr. Sec. School, Bhaisma Dist. Korba
18. Mr. S.N. Sahu (joined on 24.8.2004)	Govt. Tribal Hr. Sec. School, Sohagpur, Dist. Korba
19. Mr. Dinesh Lall (joined on 25.8.2004)	Govt. Hr. Sec. School, Kartala, Korba Dist. Korba